OBSERVATIONS ON THE ESTIMATION OF THE NEUTRALISING VALUE OF ACID CALCIUM PHOSPHATE

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In recent years, acid calcium phosphate has very largely replaced cream of tartar as the acid ingredient of self-raising flour, and the method of determining the neutralising value of this body has received attention from various workers, without unanimity of opinion having been reached. The reason for this difficulty is, as has frequently been stated, that the reaction involved is not a simple one, but several simultaneous and consecutive reactions are probably involved. These suggested reactions have been published on numerous occasions and need not be repeated here. Further, there is the difficulty of reproducing the conditions of the bakehouse in the laboratory. It is realised that any accepted method must be an empirical one under carefully controlled and standardised conditions, which will give results easily reproducible and directly applicable to baking practice.

A consideration of the literature on the successive neutralisation of the three hydrogen atoms of phosphoric acid will be of interest, as it gives information on the nature of the reactions occurring. Wendt and Clark (1923) give the following errors in the indicator method:

1. Instability and rearrangements of the phosphates produced during the course of the titration.

2. Erroneous use of phenolphthalein as indicator.

3. Use of NaOH, a strong base, whereas commercially a much weaker base is used.

They followed, electrometrically, the course of the neutralisation of phosphoric acid by calcium hydroxide. There was an in-

flection at pH 4.0, corresponding to the formation of the mono-salt, and again at pH 8.5, corresponding to the tri-salt. Irregularities occurred instead of a definite inflection for the di-salt, the curve first increasing, then decreasing, and finally increasing again; but if the solution were allowed to stand for 10 days, these irregularities were not observed and the curve was quite smooth and without an inflection. Evidently the reaction is a slow one, and time is needed for an equilibrium to be reached.

The explanation offered is that the di-salt has a transitory existence—it is formed, but breaks down to the mono- and tri-salts, the latter being precipitated.

$$4 \, CaHPO_4 = Ca_3(PO_4)_2 + CaH_4(PO_4)_2$$
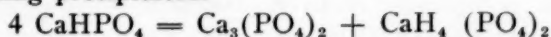
Thymolphthalein is recommended as the most satisfactory indicator. They note that as bicarbonate is higher in pH than the mono-salt but lower than the tri-salt, the latter cannot be formed; however, carbonate has a pH slightly higher than the tri-salt, so that this could be formed on heating. They state that in baking powder, the neutralisation stops short of the tri-calcium stage.

Holt, La Mer, and Chown (1925) confirmed Wendt and Clark's curves, the difficulty in reaching equilibrium, and also in the transitory existence of $CaHPO_4$. They considered that this body was precipitated, and then dissolved slowly, yielding $Ca_3(PO_4)_2$:

$$3 \, Ca^{++} + 2PO_4'' \longrightarrow Ca_3(PO_4)_2$$

This is of the 5th order, which probably accounts for its slowness.

Gortner and Hoffman (1925) followed the neutralisation of phosphoric acid with $Ca(OH)_2$ and with $NaOH$; they observed no irregularities, and stated that the two curves are not identical. The reverse titrations (using HCl) in the case of $NaOH$ follow the direct very closely, but with CaOH a "lag" is observed, which they state is not due to a time factor, but to a balanced reaction.

$$Ca_2H_2(PO_4)_2 + 4 \, HCl \rightleftharpoons 2 \, CaCl_2 + 2H_3PO_4$$
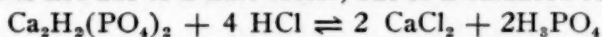
Wadman (1921) regards the higher strengths obtained by various new methods as being simply the manufacturer's selling "boost," and not scientifically accurate. Acid calcium phosphate, he says, gives an end-product "possibly an intermediate between the di- and tri-calcium salts, but nearer to the di-basic salt." Again, "the di-basic salt will not displace carbonic acid from carbonates, except under conditions far removed from those of the baking process." According to this observer, the basicity of the end-products can be increased by various expedients :.

1. Excessive dilution.

2. Indirect titration in presence of a large excess of alkali (there is never an excess in baking practice).

3. Excessive heating (1 min. at 100° C. is the maximum in baking).

4. Addition of foreign salts.

5. Small amounts of indicator (due to adsorption by the semi-gelatinous precipitate).

Wadman claims that the indirect method is completely wrong scientifically; he admits that the amount indicated by this method can be used in baking "without serious results," but the goods produced are alkaline to litmus, whereas goods made using the direct method quantities are practically neutral to litmus.

Moher (1923) recommends the following method:

Effective acidity.—"Weigh up 0.8401 grams of phosphate, add 25 cc. of cold water, and stir. Then run in 90 cc. of 0.1 N caustic soda from burette, bring to a boil and boil one minute. Add phenolphthalein as indicator and titrate back with 0.1 N hydrochloric acid. The amount of HCl required to cause the pink to disappear taken from 90 cc. of alkali used gives the neutralising value of the phosphate in terms of sodium bicarbonate and is expressed in units."

Warning (1923) recommends a method practically identical with the above.

Bailey (1925a) finds that some baking powder mixtures prepared by taking titrametric values give alkaline residues. He suggests a method of taking the pH of the residue, as well as estimating the residual CO_2. The method is as follows:

"To 26.73 parts $NaHCO_3$ add 41.77 parts phosphate to be tested and if desired 31.50 parts of starch and mix thoroly. Keep dry till used. Add 1 gram of this baking powder to 100 cc. water. Boil till CO_2 free. Cool and take pH of supernatant liquid. If the pH is other than 7.0, other powders with different amounts of phosphate must be prepared." In an example given, he finds the value by this method to be lower than that given by the A. O. A. C. method.

Again Bailey (1925b, 1926) in his reports states that further collaborative work is required on the volumetric determination of CO_2, and that results by his method of determining neutralising values have not agreed satisfactorily.

Adler and Barber (1925) emphasize the empirical nature of the titration, which does not necessarily follow baking procedure

but the conditions of which must be accurately specified—for example, the time required to reach equilibrium (see Wendt and Clark). They consider that the direct titration of the A. O. A. C. gives results too low, compared with baking results. With regard to Bailey's method, the authors criticise the acceptance of the true neutral point of pH 7.0, as the neutral point in the presence of the weak bicarbonate base.

It is shown that the di-calcium body has a neutralising and baking value, confirming that the baking powder equilibrium goes beyond the di-calcium stage. Mono-calcium phosphate (80%) is shown to have a neutral point at pH 7.89. Further, it is demonstrated that there is no relation between the residual CO_2 and the pH of the residue.

The method accepted tentatively by the Association of Official Agricultural Chemists is as follows:

> Weigh 0.84 grams of mono-calcium phosphate into a small beaker or casserole, add 25 cc. of water and 5 drops of a 0.2% solution of phenolphthalein, and titrate with 0.2 N sodium hydroxide to a faint pink; then heat to boiling; boil one minute, and continue the titration, while the solution is hot, to a faint pink colour again. (Add the bulk of the standard alkali solution rapidly and with vigorous stirring).

Logue and Ranker (1926) suggest that the titration method is not practical for comparing different phosphates, because it takes no account of the differences in the flours themselves. They had to vary the ratio of acid : bicarbonate quite appreciably with various flours to get the best baked biscuit. The pH of the satisfactory baked goods was in the range 7.0 to 7.3.

Experimental

The object of this study was to compare the two principal methods of estimation, namely, the simple direct method, recommended by Wadman, and the hot inverse method, more recently recommended by various observers. Further, Bailey's method appeared to warrant further study, particularly as it involved the actual ingredients used in practice and the measurement of the pH of the residue left after neutralisation.

It was thought that some interesting data might be obtained by following the neutralisation of a commercial acid calcium phosphate electrometrically. Although Wendt and Clark, Gortner and Hoffman, and others, have studied the curves from pure phosphoric acid, the writer has not seen any account of similar work with acid calcium phosphate as the starting material. Two high-

grade phosphate powders were obtained for this work; the measurements were carried out using a Hildebrand electrode, and the hydrogen from a cylinder was purified by passing through acid and alkaline permanganate, and then over palladiumised asbestos, heated to 800° C., and finally through a tube of silver nitrate solution, and a wash bottle of distilled water. A deci-normal calomel electrode was used as the standard half-cell. The potentiometer system consisted of a 2-volt accumulator, standard adjustable resistance, a Weston millivoltmeter, with a galvanometer as zero instrument. This apparatus was capable of accuracy to 0.05 pH.

One gram of phosphate was weighed out for each determination, about 20 cc. of distilled water was added and 1 cc. of a 1% phenolphthalein solution (bearing in mind Wadman's objection to small quantities of indicator), and the whole placed in the electrode vessel. The flow of hydrogen was started and the potentiometer reading was taken as soon as equilibrium was reached. A solution of N/5 NaOH was then run in from a burette in small quantities—either 1 or 5 cc. at a time, according to the position in the curve—the solution was well stirred and the reading taken as soon as equilibrium was established. It was noted also at what point the pink colour of the indicator appeared. When 50 cc. had been added, the burette was changed for one containing N/5 HCl, and the reverse titration carried out in a similar way, the point at which the pink colour disappeared being observed. The electrometric titration curves were plotted in the usual way.

These measurements were carried out: (a) at the temperature of the laboratory, (b) boiling, for the two phosphates, labelled "A" and "B."

These curves are given in Figures I to IV.

Phosphate A.—Considering the "cold" curves. there is a rapid increase at first, then a more horizontal portion, followed by a fairly sharp inflection, which obviously corresponds to the normal end-point of the titration. This occurs at approximately 35 cc. The reverse titration is practically identical with the direct. The "hot" curves are similar, but show no original steep portion and an ill-defined inflection at about 20 cc. The true inflection occurs at 45 cc. The main difference between the cold and the hot curves is that the hot inverse curve does not follow the "direct" during the first portion of its course, but shows a distinct lag; the "reverse" inflection occurs at 48 cc.
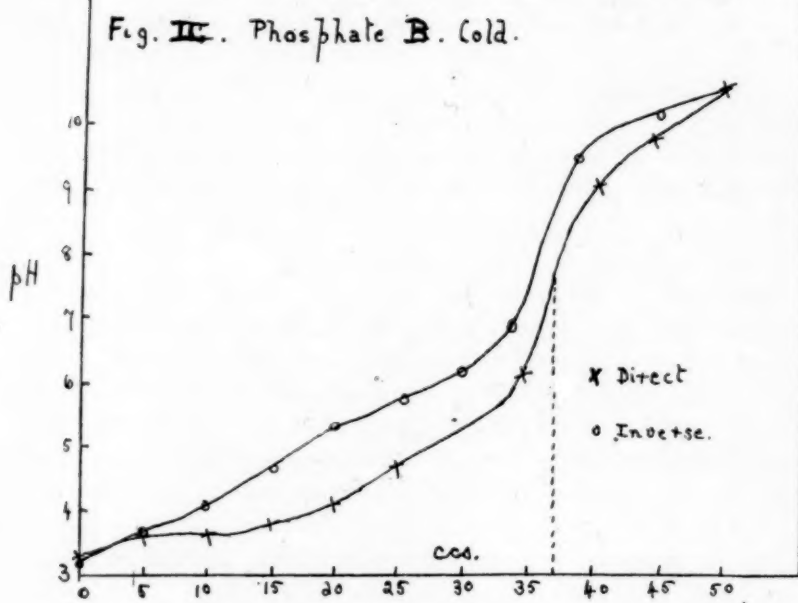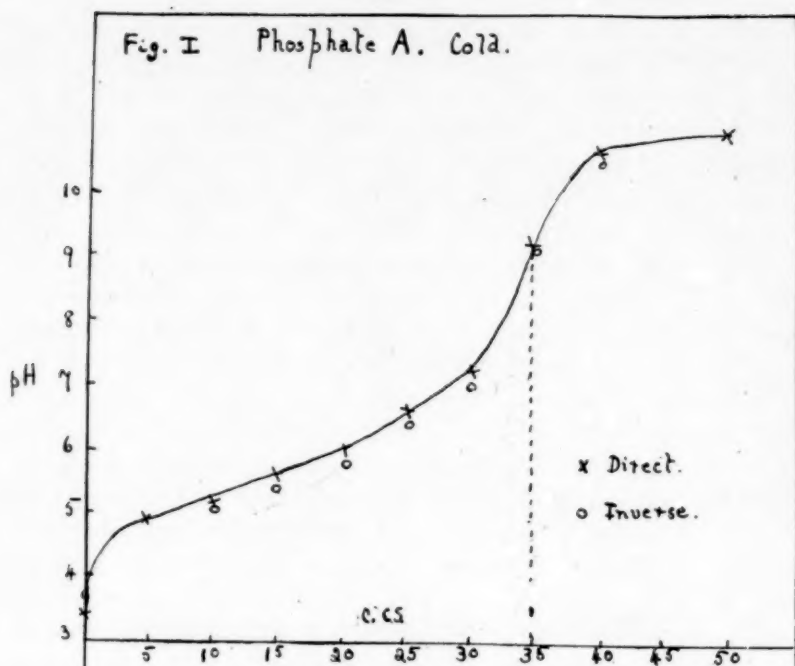
Fig. I   Phosphate A. Cold.
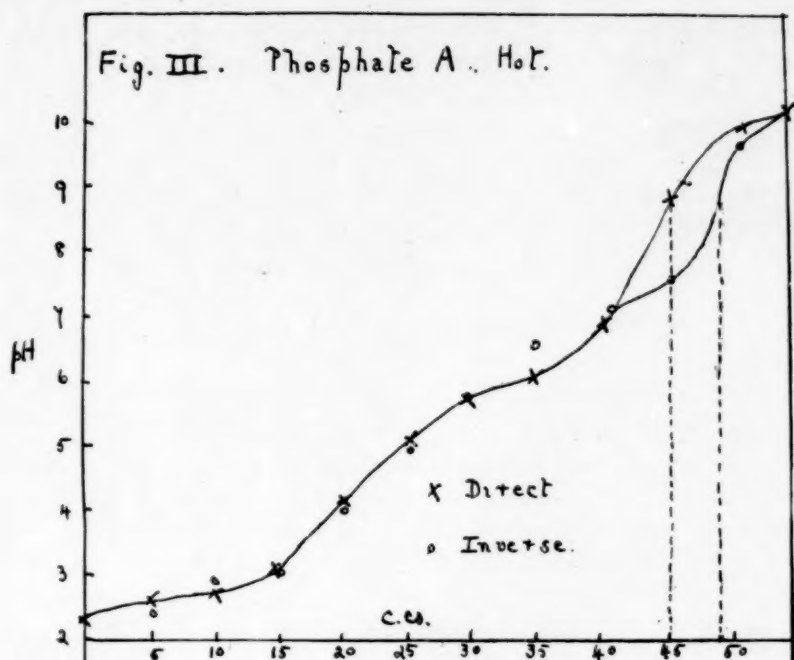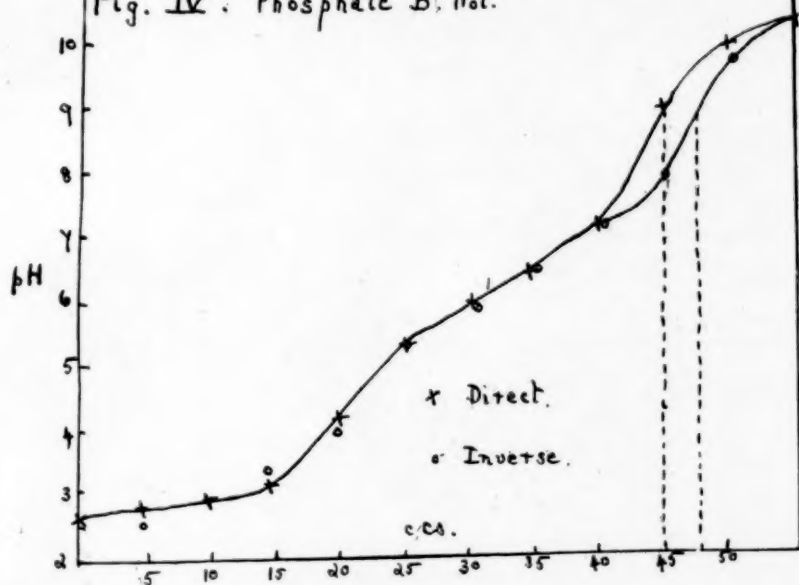
x Direct.
o Inverse.

Fig. II. Phosphate B. Cold.

x Direct
o Inverse.

Fig. III. Phosphate A. Hot.

x Direct
o Inverse.

c.cs.

Fig. IV. Phosphate B. Hot.

x Direct.
o Inverse.

c/cs.

Phosphate B.—The curves are very similar to those of Phosphate A. In the cold, however, the reverse curve lies above the direct, although the inflection is not very far removed.

In the cold, inflection occurs at ....37.0 cc.

Boiling: "direct" inflection at..................45.0 cc.

　　　　　　"reverse" inflection at ....47.5 cc.

In all cases, it was noticed that the phenolphthalein colour change takes place at the base of the inflection.

Ordinary titrations were then carried out on these samples as follows:

1. Cold direct—Wadman
2. Cold inverse
3. Hot (boiling) direct
4. Hot inverse

One gram of phosphate was weighed out for each determination, about 20 cc. of distilled water and 1 cc. of a 1% phenolphthalein solution were added.

1. N/5 NaOH solution was run in until the pink colour was permanent.

2. 50 cc. N/5 NaOH solution was added with the same quantity of phenolphthalein and N/5 HCl run in until pink colour was discharged.

3. It was raised to boiling point, the indicator added, and the N/5 NaOH run in, the titration vessel being replaced on the flame periodically.

4. 50 cc. N/5 NaOH was added, raised to boiling, the indicator added, and then titrated back with N/5 HCl until the pink colour was discharged.

The figures in Table I were obtained, given in cc. N/5 NaOH required to neutralise 1 gram of acid phosphate.

TABLE I

NEUTRALISING VALUE OF ACID CALCIUM PHOSPHATE IN TERMS OF cc. N/5 NaOH TO NEUTRALISE ONE GRAM. COLOURIMETRIC FIGURES USING PHENOLPHTHALEIN

Method	Phosphate A	Phosphate B
Cold direct	39.0	34.2
Cold inverse	43.1	34.0
Hot direct	42.5	43.9
Hot inverse	42.7	44.0

In the direct titrations (both hot and cold) the end point appeared to depend on the speed with which the titration was carried out, and variable results could be obtained.

Table II gives a summary of results on Phosphates A and B.

TABLE II

COLOURIMETRIC AND ELECTROMETRIC FIGURES FOR THE NEUTRALISING VALUE OF
ACID CALCIUM PHOSPHATES

	Ordinary titration	Electrometric Phenolphthalein	Inflection
Phosphate A	cc.	cc.	cc.
Cold direct	39.0	33.0	35.0
Cold inverse	43.1	35.0	35.0
Hot direct	42.5	37.0	45.0
Hot inverse	42.7	42.0	48.0
Phosphate B			
Cold direct	34.2	35.0	37.0
Cold inverse	34.0	34.0	37.0
Hot direct	43.9	37.0	45.0
Hot inverse	44.0	43.0	47.5

The very important observation is made that columns 1 and 2 do not agree, although both are determinations using phenolphthalein as indicator. In column 1, figures were obtained at the normal rate of a volumetric titration (i. e., adding quickly until the region of the end-point is reached), whereas those of column 2 were obtained after a slow addition, an interval being frequently allowed for equilibrium to be reached. It was confirmed that, carrying out the ordinary titration slowly (that is, adding 1 cc. and then allowing time for equilibrium to be reached), the lower figure was obtained. These results emphasize the great importance of the time factor in direct methods.

The work of Wendt and Clark has shown the difficulty of reaching equilibrium in the cold, hence the time factor noted above. This trouble is not even eliminated in the hot direct method. In the hot inverse method the two phenolphthalein figures agree fairly well but still are not in agreement with the inflection. If it be assumed that the true point of neutralisation is given by the inflection in the titration curve, then it is advisable to investigate some of the possible variants in the colourimetric method.

Variants in Colourimetric Titrations

The following were investigated:
a. Quantity of indicator
b. Amount of water added
c. Other indicators
d. Time of boiling

(a) **Quantity of indicator.**—The observations in Table III were made.

TABLE III

EFFECT ON THE NEUTRALISING VALUE OF VARYING QUANTITIES OF INDICATOR (PHENOLPHTHALEI N)

		Amount of phenolphthalein solution		Alkali required by 1 gr.
Phosphate A				
Drops		%		cc.
10 of 1.0%		0.1		42.5
5 of 1.0%		.1	(0.1 cc.)	44.0
2 of 0.2%		.2		46.0
1 of 0.2%		0.2		46.5
Phosphate B				
10 of 1.0%		0.1		44.0
5 of 1.0%		.1		45.5
1 of 1.0%		.1		47.0
5 of 0.2%		.2		47.0
2 of 0.2%		0.2		46.5

It appears that higher results are obtained with smaller quantities of indicator. This is in agreement with Wadman's criticism. but it is seen that the figures obtained with small quantities are distinctly nearer to the inflection figures. It was therefore decided to use in future two drops of 0.2% solution (in agreement with Adler and Barber).

(b) **Amount of water added, i.e., the dilution.**—Different quantities of distilled water were added, before the 50 cc. of alkali. The results appear in Table IV. The effect of dilution is apparently not an important factor.

TABLE IV

EFFECT ON THE NEUTRALISING VALUE OF VARYING DILUTIONS

Amount of water	Alkali required by 1 gr.
Phosphate A	
cc.	cc.
0	45.5
25	46.0
50	45.5
Phosphate B	
0	46.0
25	47.0
50	47.0

(c) **Other indicators.**—Wendt and Clark objected to the use of phenolphthalein as indicator and suggested the use of thymolphthalein. The writer's data show that the inflection occurs at about pH 8.3. Phenolphthalein has a dissociation constant of $K\alpha=9.7$, but being a monochromatic indicator, the change is given before $\alpha=\frac{1}{2}$, probably less than pH$=8.0$.

The following indicators were chosen from Clark's (1923) list as being possibilities, the dissociation constants being given:

Thymol blue 8.9
o-cresol sulphon phthalein 8.3
o-cresol phthalein 9.4
α-naphthol phthalein 8.4
Carvacrol sulphon phthalein 9.0

Of these, thymol blue was at hand, and being a dichromatic indicator might offer some interest. It was found that in the direct titrations again, the end-point depended on the speed and manner with which the alkali was added. However, it offered one advantage in that, using the hot method, the amount of indicator made less difference.   This is exemplified in Table V.

TABLE V

EFFECT ON THE NEUTRALISING VALUE OF VARYING QUANTITIES OF INDICATOR (THYMOL BLUE)

	Amount of indicator solution	Alkali required by 1 gr.
Phosphate A	%	cc.
5 drops (0.1 cc.)	0.04	45.5
1 cc.	.04	45.5
Phosphate B		
5 drops	.04	47.5
1 cc.	0.04	47.2

The end point was quite sharp and distinct, and in substantial agreement with the phenolphthalein figures.

(d) **Time of boiling.**—That is, the time the mixture is boiled after addition of the alkali before commencing the back titration. These effects are seen in Table VI.

TABLE VI

EFFECT ON NEUTRALISING VALUE OF VARYING TIMES OF BOILING

Time of boiling	Alkali required by 1 gr.
Phosphate A	
min.	cc.
0	45.0
1	45.5
2	46.0
5	46.5
10	47.5
15	48.0
Phosphate B	
0	46.0
1	46.5
2	47.0
5	47.5
10	48.0
15	48.0

Thus the time of boiling is a factor affecting the titration, owing probably, to the delay in reaching equilibrium; 10 minutes is probably sufficient.

Briefly, then, the nature and quantity of the indicator and the time of boiling are factors which should be specified in any standard method.

Investigations on Pure Salts

It was thought that useful information might be obtained from a study of the pure salts. Accordingly samples of the purest obtainable were procured from British Drug Houses, Ltd. These gave the following analytical figures:

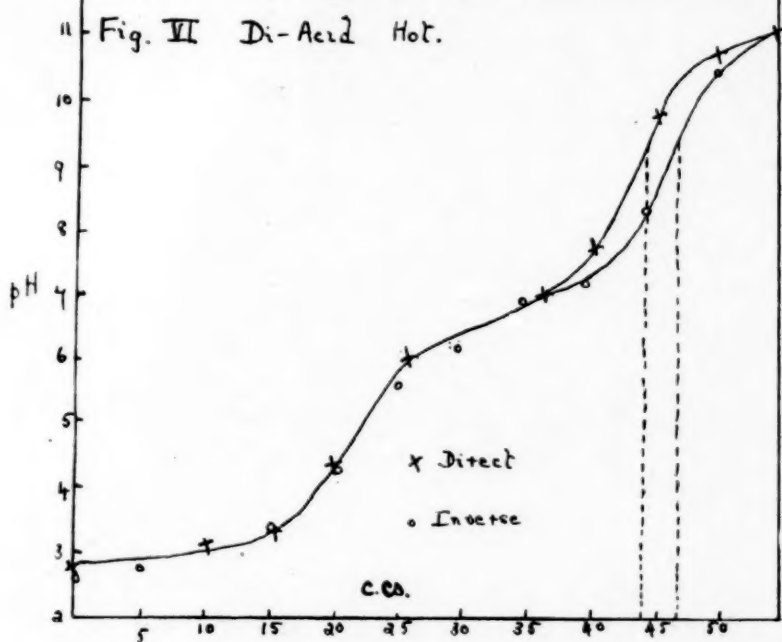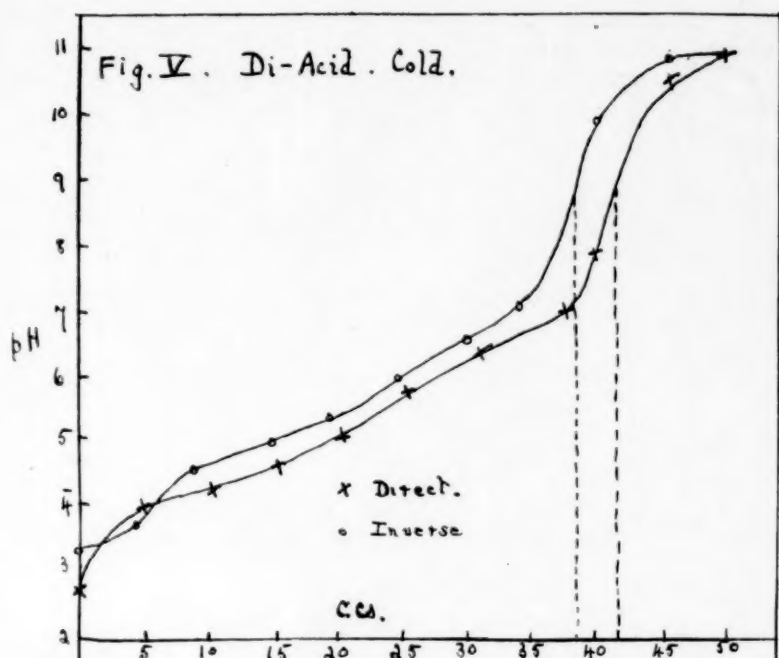|	Mono-acid %	Di-acid %
Moisture (vacuum)	3.66	0.41
P_2O_5	43.93	45.68
CaO	33.36	22.90

First, the ordinary titrations were carried out with the results given in Table VII, the amount of indicator being 2 drops, and time of boiling 10 minutes.
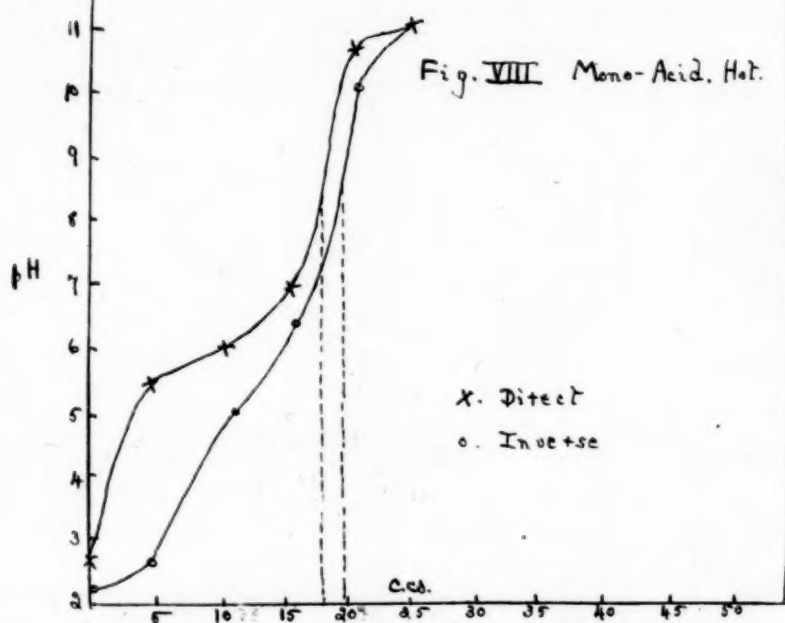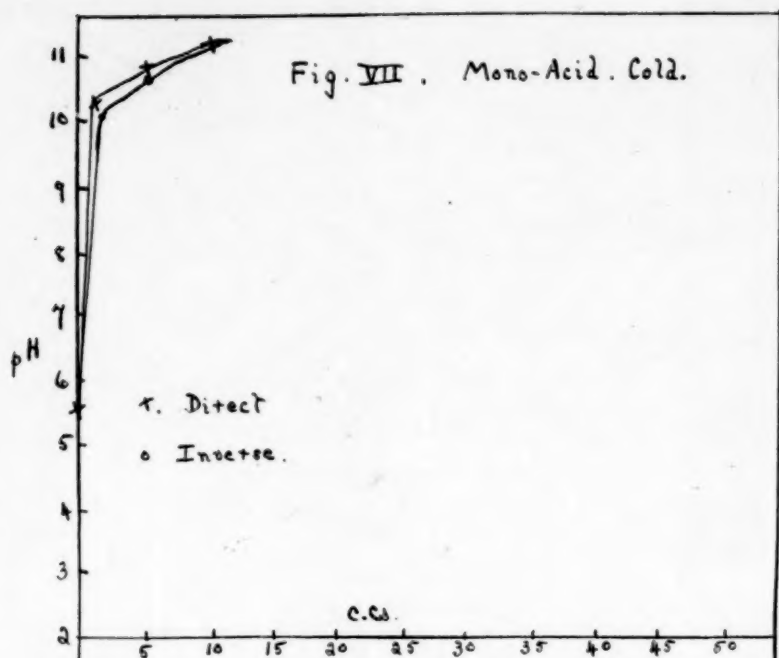
TABLE VII

COLOURIMETRIC NEUTRALISATION VALUES OF THE PURE MONO-ACID AND DI-ACID SALTS

		N/5 NaOH per 1 gr. phosphate
Di-acid salt		cc.
Cold direct	(phenolphthalein)	42.3
do	(thymol blue)	42.5
Cold indirect	(phenolphthalein)	39.0
Hot direct	do	39.4
Hot indirect	do	50.0
do	(thymol blue)	51.0
Mono-acid salt		
Cold direct	(phenolphthalein)	0.3
do	(thymol blue)	0.3
Cold indirect	(phenolphthalein)	0.5
Hot direct	do	12.8 − 16.3 on continued boiling
Hot indirect	do	20.0
do	(thymol blue)	20.0

The mono-acid salt has no neutralising power when cold; but on warming, a gradual change takes place, so that a very distinct neutralising value is obtained.

The electrometric titrations are shown in Figures 5 to 8. It will be noticed that the pH of the mono-acid salt changes from 5.6 to 2.7 on boiling. As with commercial phosphates, the cold inverse curves fall either identically with or a little below the direct, whereas the hot inverse curves are above the direct.

Fig. V. Di-Acid. Cold.

× Direct.
○ Inverse

C.cs.

Fig. VI Di-Acid Hot.

× Direct
○ Inverse

C.cs.

Fig. VII. Mono-Acid. Cold.

x. Direct
o. Inverse.

C.Cs.

Fig. VIII. Mono-Acid. Hot.

x. Direct
o. Inverse

C.Cs.

Inflections fall as under:

Di-acid   cc.

    Cold   direct 42.0

    Cold   inverse 39.0

    Hot   direct 44.0

    Hot   inverse 47.0

Mono-acid

    Cold   direct 0.5

    Cold   inverse 0.8

    Hot   direct 18.0

    Hot   inverse 20.0

indicating that the electrometric results agree with the colourimetric ones under controlled conditions. These inflections all occur at about pH 8.8.

The following important observations are summarised:

1. The mono-acid and di-acid inflections occur at the same potential.

2. The hot method gives higher results than the cold, the inverse hot method being the highest.

3. Since the baking powder reacts in the warm, the mono-acid should have some neutralising value. This acidity is apparently produced gradually as the heating proceeds.

4. The difference between the hot and the cold methods is most marked in the case of the mono-acid phosphate.

It was then decided to prepare mixtures of the two pure bodies and to titrate them colourimetrically, to determine if the presence of the mono-acid affected the readings quantitatively. The figures obtained are given in Table VIII.

TABLE VIII

COLOURIMETRIC NEUTRALISING VALUES OF MIXTURES OF THE MONO-ACID AND DI-ACID SALTS

% Di.	Mixture % Mono	Cold direct	Hot inverse
90	10	36.0 (38.3)	47.5 (47.0)
80	20	33.6 (34.4)	44.3 (44.0)
70	30	26.3 (30.5)	42.0 (41.0)
60	40	22.0 (26.6)	39.2 (38.0)
50	50	18.4 (22.6)	36.0 (35.0)

*Figures are given in cc. of N/5 NaOH required by 1 gram phosphate mixture. In parentheses are given the calculated titrations for the respective mixtures.

In the cold, the observed values are lower than the calculated, but in the hot inverse method there is better agreement, the observed values being slightly higher in most cases.

Bailey's method.—This method, as has been pointed out by Adler and Barber, is in reality the determination of various points in the titration curve, and as such is to be commended, particularly as it involves the same reagents as are actually used in baking,

i. e., acid phosphate and sodium bicarbonate. Bailey takes as his "neutral" point, the true neutrality of pH 7.0. Adler and Barber criticise this on the ground that hydrolysis is sure to take place, so that at the actual neutrality the pH will be somewhat higher, and they suggest a figure of pH 7.89.

The present work would suggest a still higher figure using NaOH as the base; the curve is steep, so that it is not possible to give an accurate figure.

Bailey's method, but without any starch present, was then applied to six phosphates: A, B, mono-acid, and di-acid, as above, and two other commercial phosphates, "C" and "D." The "neutralisation" values on the hot inverse method were used for the basis of the mixing, with the results given in Table IX.

TABLE IX

RESIDUAL pH OF NEUTRALISED MIXTURES OF ACID CALCIUM PHOSPHATES AND SODIUM BICARBONATE

Phosphate	Proportions	pH
A	0.57 acid 0.43 bicarbonate	7.3
B	0.56 acid 0.44 bicarbonate	7.4
C	0.55 acid 0.45 bicarbonate	7.3
D	0.57 acid 0.43 bicarbonate	7.48
Mono-acid	0.74 acid 0.26 bicarbonate	7.65
Di-acid	0.54 acid 0.46 bicarbonate	7.3

Thus it is seen that using sodium bicarbonate the neutral point occurs between pH 7.3 and 7.4 in the majority of cases, with an average of 7.40. The effects of excess acid and alkali are indicated in Table X.

TABLE X

EFFECT OF ADDITIONAL ACID AND ALKALI ON THE RESIDUAL pH OF MIXTURES OF ACID CALCIUM
PHOSPHATES AND SODIUM BICARBONATE

Phosphate C used	Proportions	pH
Additional acid	{ 0.56 acid 0.44 alkali	7.2
	{ 0.59 acid 0.41 alkali	6.98
Additional alkali	{ 0.54 acid 0.46 alkali	7.9
	{ 0.52 acid 0.48 alkali	8.86

A small excess of acid does not shift the pH very far, whereas a slight excess of alkali makes a very appreciable difference. This is an important point, practically, and suggests the advisability of having a raising mixture with a small excess of acid over the amount given by the hot inverse method. These figures show that, provided a figure of pH 7.40 is taken, Bailey's method can be used to determine the neutralising value of an acid phosphate, in tolerable agreement with the hot titration method; further, if another pH be taken, probably about 6.7, then the values will agree with the cold direct method. In the presence of a large quantity of the di-calcium salt, however, the pH of the neutral point appears to be slightly removed to the alkaline side thus

the mono-acid body gave a figure of pH 7.65

a poor quality phosphate (E) gave a figure of 7.60

using the hot titration ratios.

Baking results.—From observations commercially it has been found that the following raising mixture gives satisfactory results:

5 lb. (80 %) acid phosphate }
                             } in 1 sack (280 pounds) of flour
3½ lb. sodium bicarbonate }

This is approximately in the ratio

{ 0.60 acid phosphate
{ 0.40 bicarbonate

which means an excess of acid over that given by the hot neutralisation method.

The pH of such mixtures was determined, as given in Table XI.

TABLE XI

RESIDUAL pH OF MIXTURES OF ACID CALCIUM PHOSPHATE AND SODIUM BICARBONATE
FOR OPTIMUM BAKING VALUE

Phosphate	Proportions	pH
A (80%)	0.60 acid 0.40 bicarbonate	7.05
B (80%)	0.60 acid 0.40 bicarbonate	6.95
C (82%)	0.59 acid 0.41 bicarbonate	6.98
D (80%)	0.60 acid 0.40 bicarbonate	6.98
Di-acid (84%)	0.58 acid 0.42 bicarbonate	6.98

If, therefore, Bailey's method be applied to a figure of pH 7.0, as he suggests, a mixture is obtained which gives satisfaction in baking.

Turning now to the mono-acid body, scones were made, using this as the acid ingredient in the following proportions:

(a) 10 gm. mono-acid phosphate
2 gm. bicarbonate } to ½ lb. flour

(b) 15 gm. mono-acid phosphate
2 gm. bicarbonate } ditto

(a) gave fairly good raising power, but the inside colour was distinctly yellow, indicating an excess of bicarbonate. (b) was completely satisfactory, and gave a scone equal to those using good grade di-acid phosphate.

The above satisfactory ratio is approximately
{ 0.88 acid
0.12 bicarbonate } which on Baile 's method gives pH 6.20

The ratio given by the hot inverse method is
{ 0.75 acid
0.25 bicarbonate } giving pH 7.65 on Bailey's method

which, obviously, is much too great an excess of alkali.

It is confirmed that the mono-acid body does possess some neu-
tralising properties, as indicated by Adler and Barber, but that it
is not as high as given by the hot inverse titration. In applying
the Bailey method, a pH of 6.2 must be aimed at in order to give
a satisfactory baking mixture, when using 100% mono-acid phos-
phate.

The pH (electrometrically) was taken on a number of baked
scones; one of these was made from the above commercial rais-
ing mixture, and the others were either purchased from a commer-
cial bakery, or made from self-raising flours on the market.

The range was from pH 6.55 to pH 6.85, with an average of
6.60. This is not in agreement with the figure obtained on the
original raising mixture (known in only one case) or with the fig-
ures of pH 7.0 to 7.3 given by Logue and Ranker for baked biscuits.
Smith and Bailey (1923), however, have determined the pH of
biscuits made with various commercial powders, and found very
large discrepancies, namely pH 5.84 to 7.76. The figure 5.84 was
obtained with a cream of tartar powder and 7.76 with a mono-
calcium phosphate powder, but no details of the composition of
these powders were given.

Discussion

It must be realised, in view of the well-recognised complexity
of the reaction, that it is almost impossible to get a definite and
scientifically accurate neturalisation value; an equilibrium is in-
volved, or probably more than one equilibrium, so that any figure
obtained must of necessity be a function of the conditions. The
aim must, therefore, be to select a set of conditions which will
give consistent and reliable results. These conditions need not be
exactly those of the baking test, the fulfillment of which in the
laboratory would be difficult, but must be easily applicable to bak-
ing practice.

The irregularities in Wendt and Clark's curves indicate the
difficulty of attaining the equilibrium in the cold, unless long time
is allowed for the reaction. Again, the observation made above,
that the speed of the titration is an important feature, rather points
to the conclusion that such results are not truly reproducible.
Further, it has been confirmed that the mono-acid does possess a
neutralising value in the baking process, whereas results in the
cold suggest its inactivity. It is probable that the di-salt is
formed, but slowly breaks down to form the tri-salt, with libera-

tion of a H ion. The exact mechanism of the reaction is not definitely understood. It is this slow breaking down process which causes the delay in reaching the equilibrium. Presumably, using a fairly strong base, the final stage will be the tri-basic salt, but it is generally agreed that in the baking oven this stage is not reached, but an equilibrium between the di-acid and tri-acid salts. It is not to be hoped to produce this same equilibrium during the titration, but the cold method does not yield an equilibrium, except after a time too long for normal usage. The fact that the inverse curves are practically identical with the direct suggests that excess of alkali does not hasten the reaction.

It might be supposed that at the boiling temperature the reaction would be accelerated, but the hot direct method suffers from the same drawback as the cold direct, namely, that the speed of addition of the alkali affects the result.

Coming now to a consideration of the hot inverse method, this, undoubtedly, gives the highest result of all, and in that fact is found Wadman's condemnation; however, it does give a definite and reproducible figure, and the electrometric inflection agrees with the colourimetric end-point, so long as the ordinary titration is carried out under conditions which admit the attainment of the final stationary point. In confirmation of this may be given the figures for three other commercial phosphates "C" "D" and "E."

TABLE XII

COMPARISON OF NEUTRALISING FIGURES, COLOURIMETRICALLY AND ELECTROMETRICALLY, OF THREE COMMERCIAL PHOSPHATE POWDERS

Phosphate	Inflection	Using phenolphthalein colourimetrically	Using thymol blue colourimetrically
	cc.	cc.	cc.
C	49.5	48.7	49.0
D	46.0	45.5	46.5
E	28.5	27.0	28.0

Viewed in the light of Bailey's method and of practice, this hot inverse titration gives results which are too high, that is, more acid is required than is indicated by this titration. This "neutral" mixture gives a pH of 7.4, whereas for satisfaction in baking, a mixture giving a residual pH of 7.0 is required. May not this difference be due to the fact that in the titration with NaOH, the final stage is reached, whereas in the baking powder mixture the neutralisation stops short at an equilibrium between the di- and tri-salts.

In the opinion of the writer, the great advantage of this hot inverse method is that a *definite* neutralisation point—a real end-point—is reached. Having obtained this property of a phosphate powder, allowance can be made in such a way that the baking ingredients are mixed with an "excess of acid," so that a residual pH of 7.0 is obtained. It is possible to use this "end-point" mixture in baking, but the goods produced therefrom are apt to be very near the alkaline side. The cold method, however, goes too far on the acid side. The most satisfactory mixing gives a final product with a pH 6.60.

Bailey's method has the great advantage of using the actual baking ingredients; it does not appear to lend itself to a direct determination of the neutralising value of a phosphate powder, but it should provide a very useful means of adjusting the hot inverse method to baking practice. In other words, its great usefulness is in that it gives an accurate and quick method for checking the correct mixture of the raising ingredients.

The recommendation is therefore made that the hot inverse method be used for evaluating an acid phosphate. It has been shown that there are two important factors influencing the colourimetric reading, but if these be controlled, the titration agrees with the electrometric inflection. Phenolphthalein or thymol blue can be used as indicator, although with the former, the quantity of the indicator must not be too great. The time of boiling makes a small difference, but after 10 minutes a constant value is obtained, the final and complete neutralisation having, apparently, been attained.

In view of the considerations in this paper, it might be advisable to review Wadman's severe censure. The writer is in agreement with him on a number of points. In the first place, it is quite beyond the accuracy of the titration to suggest taking the weight to the fourth decimal place. The criticism that the hot inverse method, using an excess of alkali, is entirely foreign to the baking procedure is admittedly justified, and the same applies to the long time of boiling, whereas the goods are probably only submitted to this temperature for a much shorter time. Surely this last criticism applies to the cold method, but in the opposite direction. Wadman's explanation, that the higher results obtained with small quantities of indicator, as an adsorption by the gelatinous precipitate, does not appear to be confirmed by the present work, nor is excessive dilution found to affect the titration appreciably.

Proposed Method

Weigh out 0.84 grams of phosphate and place in a conical flask. Add 25 cc. of cold water, mixing thoroughly by rotating the flask, and then add 90.0 cc. of 0.1 N sodium hydroxide. Bring the solution to the boil and boil for 10 minutes. Add a few drops of thymol blue 0.04% solution (or not more than 5 drops (0.1 cc.) of a 0.2% phenolphthalein solution) and titrate with 0.1 N hydrochloric acid until the indicator change is observed, keeping the solution boiling.

Subtract the amount of acid used (cc.) from 90 and the difference is the *limiting* neutralizing value of 100 parts of the acid phosphate in terms of parts of sodium bicarbonate.

In order to obtain the *baking* value of the acid phosphate, mix the two ingredients in the above proportions; take one gram of this mixture and add 100 cc. of water. Boil till CO_2 free, cool, and take pH of the supernatant liquid. Then adjust the mixture until the residual supernatant liquid gives a pH of 7.0. This then gives the best ratio of acid phosphate: sodium bicarbonate for satisfactory baking.

Summary

A comparison is made between the electrometric and colourimetric titrations of two acid phosphate powders.

It is shown that the normal cold titration is dependent upon the rate of addition of the alkali and consequently is not satisfactory.

The hot direct method suffers from the same disadvantage.

In the hot inverse method, the colourimetric end-point agrees with the electrometric inflection, if the following conditions are observed.

    (a) Thymol blue used as indicator, or a small quantity of phenolphthalein.

    (b) The mixture is heated until equilibrium is reached.

The result of this method gives a figure which is too high for commercial practice, but is characteristic of that particular phosphate powder.

Bailey's pH method is useful for checking the correct mixture of a raising powder, and can with advantage be used to correlate the above titration figure with the most satisfactory acid phosphate: sodium bicarbonate ratio for baking practice.

The pH of satisfactory baked scones is 6.55 to 6.85.

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ESTIMATION OF FAT CONTENT OF FLOUR AND MILLING STOCKS

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There appears to be little doubt that the fat content of flour and milling stocks is almost invariably estimated by a Soxhlet extraction with ether, but there is far from unanimity among cereal chemists as to whether or not the stock should be dried before extraction.

The tentative method of the American Association of Cereal Chemists requires the "thorough" drying of the flour before the estimation, and the official method of the Association of Official Agricultural Chemists states "Extract about 2 grams of the sample, dried as directed, with anhydrous ether for 16 hours."

Various investigators have extracted the fat from flour and have studied its properties, among whom may be mentioned Frankforter and Harding (1899), who report that above 100° C. the oil changes colour, becoming reddish-brown.

De Negri (1898) obtained his oil by expression, but no attempt was made to get a quantitative yield, only about 80% of the estimated total being obtained.

Paul (1921), working with oats, dried to a moisture content of 4% at 36° C. before extraction with petroleum ether. He reports that if the extracted oil be kept at 99° C. for several days it becomes hard and loses its mobility.

Jacobs and Rask (1920), in their study, used the official method and obtained the distribution of the oil between the bran, germ, and inner endosperm, as follows:

Commercial bran	3.58%
Commercial germ	10.02%
First middlings flour	0.75%

They caclulated that, theoretically, patent flour, as the purest stock, should contain 0.75% fat. They suggest the fat content as a measure of the amount of germ in the various stocks.

Ball (1926) states that the oil obtained by expression from the embryo was lighter in colour than that obtained by ether extraction, although the drying of the latter was carried out in an atmosphere of carbon dioxide.

Greville (1923) pointed out the difference in the amount of fat extracted from flour with and without preliminary drying, and suggested that some volatile portion of the fat was lost in the water vapour during the drying. He claims to have recovered some of this "lost" fat from the water vapour driven off.

Kent-Jones (1924) states "In comparing two analysts' reports on fat contents in flour, it is essential to remember under what conditions the estimations were made. The main source of difference is the moisture. If the flour be dried first, the result will almost invariably be about half that if the ether extraction be done straight away on the flour as it is. Which is the true figure? Which is the figure usually accepted in the trade?"

It therefore appeared to be of some importance to follow this problem further, in the hope of throwing some light on the reason of these differences. Kent-Jones has suggested that the drying may cause oxidation of a portion of the fat.

Experimental

Three flours from a South of England mill were obtained for this study; the fat content was determined by the method given by Kent-Jones, but the time of drying in a water oven at 98° C. was varied. The refractive index at 20°C. was taken on these fats after the evaporation of the ether, but without any attempt to get rid of the last traces of ether or water; and again after drying for 2 hours at 98° C. The flours were:

A commercial patent flour
A commercial lower grade flour
Flour from "J" machine (richest in germ).

TABLE I
AMOUNT OF FAT EXTRACTED AND REFRACTIVE INDEX OF THE FAT AFTER VARIOUS PERIODS OF DRYING

| Patent | | | Refractive index | |
Time of drying	Moisture lost	Fat	Undried	Dried 2 hours
Hours	%	%		
nil	.....	0.97	1.4750	......
1	12.04	0.98	......	......
6	13.23	0.95	1.4732	1.4890
16	14.20	0.87	......	1.4890
Lower grade				
nil	.....	1.50	1.4770	1.4888
1	11.09	1.55	1.4718	1.4883
6	13.78	0.94	1.4840	1.4880
16	13.95	0.85	1.4690	1.4875
"J" machine				
nil	.....	2.26	1.4660	1.4800
1	12.36	2.28	1.4660	1.4835
6	13.00	1.98	1.4690	1.4795
16	13.58	1.39	1.4620	1.4830

It is apparent that the first hour's drying, which removes at least 80% of the moisture from the stock, does not affect the amount of fat extractable by ether—in fact, there is a slight increase over the undried in all cases; after the removal of the last 1 or 2%, however, the fat extracted diminishes with the time of heating.

From the view point of the "steam distillation theory," it would be anticipated that the largest loss of fat would occur during the removal of the majority of the water. The above results show that the greatest loss is sustained as the last traces of water are removed. While no evidence is produced to indicate the nature of the changes, these figures lead to the conclusion that some change, possibly as Kent-Jones suggests, of an oxidation nature, takes place as the flour or stock is dried, and that the rate of change becomes progressively greater as the moisture content diminishes. In all probability this change is one that renders the fat insoluble in ether. An attempt to find a solvent for this changed fat is referred to later.

The refractive indices obtained before drying were very variable, owing undoubtedly, to varying amounts of ether and water retained because, as previously mentioned, no attempt was made to free the fat of these at that stage. The refractive index after drying in the water oven at 98° C. for two hours approached in all cases the value 1.4890. In the patent flour with the smaller quantity of fat, this value is reached in the two hours allowed, but in the "J" fat, this value is not reached, although a distinct increase is noticed over the "undried" values. These results indicate that the fat extracted by ether changes gradually as it is dried, the extent of the change depending on the time of heating and the amount of fat. The appearance of the fat changed also during the drying. It slowly became darker in colour and less mobile, similarly to Paul's oat fat—and in the case of the smaller quantity, i.e., the patent fat, it became hard and horny. It was observed that this semi-solid fat was practically insoluble in ether, i.e., in its original solvent.

In all cases, it was noticed that the flour was much whiter after extraction than before, owing probably, to the removal of the chromolipoid colouring matters of the flour, carotin and xanthophyll (Bailey 1925), with the fat. It was suggested that if this extracted flour were dried there would be less discolouration, assuming that the oxidation of the flour during drying be due to the fat, its associated colours or other substances soluble in ether.

Accordingly the following experiment was performed: A straight-run flour was divided into two portions

(A) was extracted in a Soxhlet for 8 hours with ether. Then exposed to the atmosphere of a room for 16 hours (overnight).

(B) was exposed to the same atmosphere for the same period. Moistures were then determined on 10-gram samples in the water oven at 98° C.

TABLE II

LOSS IN WEIGHT OF EXTRACTED AND UNEXTRACTED FLOURS DURING DRYING IN WATER OVEN AT 98°C.

Time in oven	Loss in weight of 10 grams	
hours	A	B
	gm.	gm.
6	1.325	1.293
24	1.392	1.389
30	1.338	1.334
48	1.341	1.334

The two sets of figures are parallel, the moisture lost after 24 hours being

A 13.92%
B 13.89%

which are within experimental error.

During the next six hours, there was a gain in weight in each case,

A 0.54%
B 0.55%

being again practically identical results. Thereafter there was little change in either figure. After 48 hours the ether-extracted sample, A, was only very slightly darker in colour, whereas the ordinary sample, B, was quite deeply coloured, as is usual.

These results indicate that after the extraction of the fat and colouring matter, oxidation or dextrination still takes place in the flour on prolonged heating, and to practically the same extent as in the unextracted flour. Changes in the fat and colouring matters are not responsible for the gain in weight of a flour after it has dried out, although they are responsible for the darkening in colour.

It was thought necessary to study the refractive index figures somewhat further. A quantity of fat was obtained from "J" machine flour by successive ether extractions in a Soxhlet apparatus. The ether was driven off on the water bath in a current of air and the refractive index taken in an Abbé refractometer at 20° C. The fat was then placed in a water oven at 98° C. for several days, and the refractive index noted periodically. During drying, the fat grad-

ually solidified and turned a dark brown colour; at the end of two days it had the appearance of a brown dried jelly. The figures are given in Table III.

TABLE III

REFRACTIVE INDEX OF WHEAT FLOUR FAT AFTER VARYING PERIODS AT 98°C.

Time in oven	Refractive index
hours	
nil	1.4830
1	1.4865
6	1.4882
12	1.4885
24	1.4890
48	1.4890

There is thus a gradual increase in the refractive index as the heating is continued, simultaneous with the thickening of the fat. With a larger quantity of fat the same figure is reached eventually as found previously.

A further experiment was conducted as follows: 10 grams of "J" flour were dried in the oven for 1 hour and then the oil was extracted with ether for 8 hours in the usual way, the last traces of solvent being driven off in an oven at 40° C. The weight of the oil was then taken as well as the refractive index. Subsequently it was heated at 98° C. for periods of 15, 30, 60, and 120 minutes, the change in weight and refractive index being taken at the end of each period (corrections being made for the loss of fat removed for the refractometer reading). Thereafter the weight was practically constant.

TABLE IV

CHANGES IN WEIGHT AND REFRACTIVE INDEX OF A WHEAT FLOUR FAT DURING HEATING AT 98°C.

Time interval	Change in weight	Refractive index
min.	gm.	
nil	......	1.4827
15	−0.009	1.4840
30	−0.0074	1.4850
60	−0.0052	1.4855
120	−0.0105	1.4860

This shows that the fat is not dried to "constant weight" until two hours at 98° C. and also that there is no gain in weight during the change in properties, as might be expected if it were an oxidation. Spaeth, according to Ball (1926), has suggested that, during heating of the fat, unsaturated acids may become polymerised.

From the above work it is seen that the refractive indices of wheat oil are

1. without heating to a high temperature 1.4830
2. after completely changed at 98°C. 1.4890

Other observers have given the following:

TABLE V

REFRACTIVE INDEX OF WHEAT FLOUR FAT FROM DIFFERENT OBSERVERS

Observer	Refractive index	Portion extracted
Spaeth (1894)	1.4851 (25°C.)	Flour
De Negri (1898)	1.4750 (25°C.)	Embryo
Frankforter and Harding (1899)	1.48325 (20°C.)	Embryo
Ball (1926)	1.4686	Embryo
	1.4714	Flour

An attempt was made to find a suitable solvent for this altered fat, but without success. It appeared practically insoluble in any of the following organic solvents: ether, petroleum ether (60-80° C), petrol, carbon tetrachloride, and 90% ethyl spirit.

It is probable that the change in mobility and properties which takes place on heating the extracted fat for several hours at 98° C. is parallel with that change which rendered the fat non-extractable from the flour after it has been dried for a considerable period.

Suggested Method

Flour or milling stock is dried for one hour in a water oven. It is then transferred to a Soxhlet thimble and extracted in a Soxhlet apparatus for 8 hours, with anhydrous ether. The ether solution is filtered into a tared flask, the filter paper being well washed three times with fresh ether. The combined ether and washings are evaporated to dryness on the water bath and finally for two hours in an oven at the temperature of boiling water.

Summary

1. Less fat is extracted by ether from completely dried flour and stocks than from moist or partly dried stocks.

2. The lower fat content found in flour after drying is not due to loss in "steam distillation" as suggested.

3. The discolouration of flour on drying is probably due to a change in the fat or associated material, but this change does not account for any gain in weight.

4. Values for the refractive index of wheat oil are given.

5. The change in the fat is probably not an oxidation, but possibly an internal alteration, the nature of which was not determined.

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PRE-HARVEST FACTORS WHICH AFFECT WHEAT QUALITY

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(Read at the convention, June 3, 1927)

The quality of wheat is influenced to a very large extent by the soil and climatic environment to which the plant is subjected. From the time the wheat is seeded until the grain is harvested, variations in soil and climatic conditions are constantly influencing the quality of the crop.

The quality of the harvested crop is not due to the influence of any single factor, but rather to several interacting factors. The study of the effect of climatic variations is particularly difficult, as it is practically impossible to secure ideal experimental conditions in which the effect of all factors except the one studied can be eliminated. A study of the effect of soil fertility is simpler, as in this case climatic factors can be made a constant for at least one year or season.

When studying variations in quality of any substance, some measures of quality are necessary. In this study the principal ones used are (1) the test weight per bushel and (2) the protein content of the wheat. The test weight per bushel relates to the milling quality of the wheat and color of the flour, while protein content

affects the baking strength of the flour. The discussion will deal
with hard bread wheats, and particularly with hard red spring
wheats.

Effect of Variety

An extended discussion of varieties and types of wheat is not
permissible. It is necessary, however, to call attention to the fact that
different types and varieties of wheat have certain inherent charac-
teristics which are not essentially altered by climate and soil. Re-
sistance to such diseases as black stem rust may have an im-
portant influence upon quality, particularly the test weight. Some
varieties of wheat will consistently produce grain of higher pro-
tein content than others, when grown under identical conditions.
The type of gluten also varies considerably between different
varieties and types of wheat. Durum wheats, for example, contain
gluten which is evidently unsatisfactory for a strong bread flour,
but is peculiarly suitable for macaroni and similar paste products.

It is essential, therefore, that suitable varieties of wheat be
used, as evidently no combination of soil and climate can essentially
change the inherent characteristics of a variety or type of wheat.

Effect of Seed

Assuming that the seed used is of suitable variety, and is free
from foreign materials and disease, the source of seed and the
quality as measured by test-weight and protein content do not
influence the quality of the crop.

The "tri-local" experiments of the United States Department
of Agriculture in co-operation with the Kansas and California
stations showed that climatic conditions were more important
than seed or soil in determining the protein content of wheat.
LeClerc (1910) concludes from these experiments: "Wheat of the
same variety obtained from different sources, and possessing widely
different chemical and physical characteristics, when grown side
by side in one locality, yields crops which are almost the same in
appearance and composition."

Thatcher (1913), of the Washington station, also found that
the protein content of the seed did not influence the protein con-
tent of the crop.

Stoa and Mangels (unpublished data) of the North Dakota
Agricultural Experiment Station have recently repeated the work
of previous investigators by seeding Marquis wheat which varied
in test weight and protein content. The results of these tests in

1926 were negative, that is, the test weight and protein content of the wheat had no influence on the test weight and protein content of the resulting crop.

Two lots of Marquis wheat were seeded in 1926 which varied approximately seven pounds in test weight per bushel (55 to 62 pounds). The crops from the two lots of seed showed a small difference in test weight, and in this case the light seed produced the heavier wheat.

Eight lots of Marquis wheat, varying in protein content from 10.19% to 14.44% were seeded in 1926. Table I and Figure 1 show the results from this experiment.

TABLE 1

EFFECT OF PROTEIN CONTENT OF MARQUIS SEED ON PROTEIN CONTENT OF CROP

Sample	Source of seed	Protein in seed	Protein in crop
		%	%
A	Fargo variety plots, Ser. 3, 1924 crop	10.19	14.03
B	Alberta, Canada	10.32	13.93
C	Dekalb, Ill.	10.81	13.97
D	Montana	11.37	14.19
E	Saskatchewan, Canada	11.85	13.86
F	Montana	11.83	13.97
G	Fargo variety plots, Ser. 2, 1923 crop	13.18	13.93
H	Fargo variety plots, Ser. 2, 1924 crop	14.44	13.96
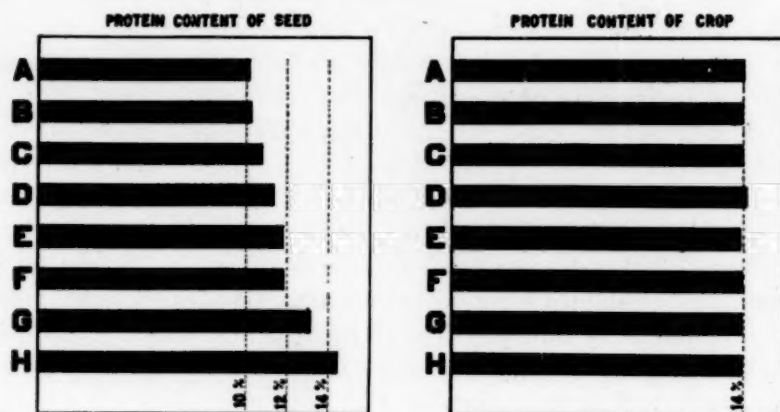
Fig. 1. Effect of Protein of Seed on Protein in Crop
Seeded and Harvested at Fargo in 1926

Figure 1 shows that the protein content of the seed has no influence on the protein content of the resulting crop. The seed varied in protein content from 10.19% to 14.44%, but the resulting crops varied only from 13.86% to 14.19%. Variation between the eight samples was not in line with variation of protein content in

the seed. The seed of lowest protein content (10.19%) produced wheat with a protein content of 14.03% while that with the highest protein content (14.44%) produced wheat having a protein content of 13.96%.

Effect of Climatic Factors

The type and quality of wheat which may be produced in any given agricultural area is determined largely by climatic conditions. Whether winter or spring wheats shall be used is determined by average winter temperature and the relative amount of snowfall. Rainfall and temperature determine whether hard or soft types of wheat may be produced.

When studying the effect of climate on wheat quality, the two principal climatic factors to be considered are temperature and rainfall. The quality of wheat is due largely to a combined influence of these two factors, except that in some cases soil fertility may have a significant influence. Rainfall and temperature have different effects, and each may often counteract the influence of the other.

The North Dakota Experiment Station has data on test weight and protein content of spring wheat covering several years, and for the last five years these data have been obtained by a crop survey made immediately after the wheat was harvested.

Test Weight Per Bushel

Figure 2 shows the average test weight of North Dakota hard red spring wheat for ten years (1917 to 1926); also the mean temperature for June and July and the rainfall during the growing season for the same years.

The temperature shows relatively greater seasonal variation than the rainfall (Fig. 2). Relatively low average test weights are shown in 1919, 1920, 1921, and 1923. The mean July temperature for 1919, 1921, and 1923 is above 70°F. and for 1920, 68.3°F. The highest average test weight is found in 1924, when both June and July temperatures were low. The records for these years indicate, therefore, that a relatively low temperature during the latter part of the growing season tends to produce heavy wheat.

The years 1917 and 1926 both show mean July temperatures above 70°F., and also a relatively high average test weight per bushel. However, the seasons of 1917 and 1926 were relatively very dry and the June temperature for both years was low.

High temperatures during the latter part of the growing season will probably adversely affect the test weight in two ways.

The direct effect of the higher temperature is to hasten maturity and dry up the grain before the heads are completely filled; the indirect effect is the growth of wheat stem rust. Wheat rust requires both heat and moisture for rapid development, and in such seasons as 1917 and 1926 the crop matures without serious rust injury. Owing to low rainfall and consequent low humidity, the relatively high July temperatures in 1917 and 1926 did not favor rust development, as in 1919, 1920, 1921, and 1923. The low June temperatures in 1917 and 1926 retarded rust development and probably to some extent counteracted the direct effect of the high July temperatures.

The principal climatic factor influencing the test weight is evidently the prevailing temperature during July. Rainfall does not appear to be an important factor, but low rainfall may counteract the detrimental effect of heat.
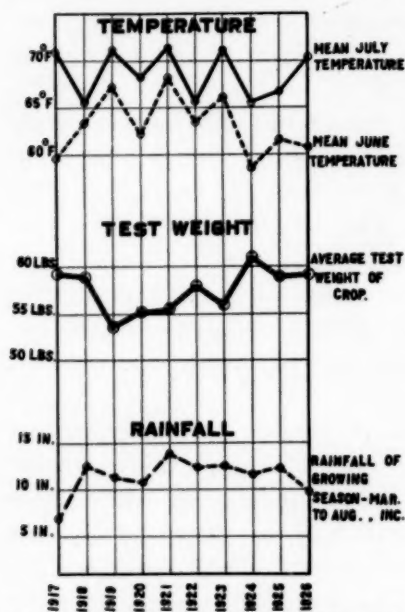
Fig. 2. Temperature and Rainfall and Test Weight per Bushel of Hard Red Spring Wheat Grown in North Dakota
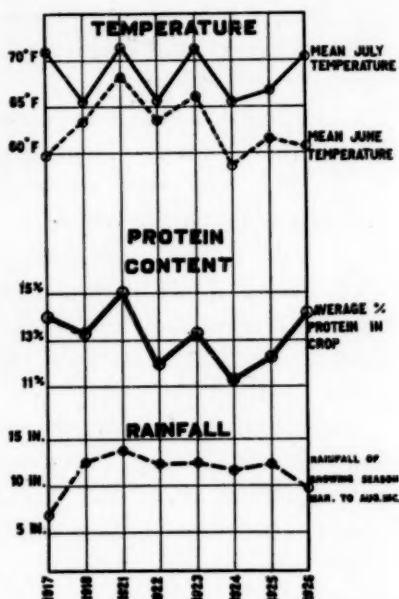
Fig. 3. Temperature and Rainfall and Protein Content of Hard Red Spring Wheat Grown in North Dakota

Protein Content of Wheat

Figure 3 shows the average protein content of North Dakota hard red spring wheat for eight years[1] (1917 to 1926); also the mean temperature for June and July and the rainfall during the growing season for the same years.

1 Data on protein content of wheat for 1919 and 1920 were not sufficient for comparison.

Temperature, especially July temperature, again appears to be the important climatic factor. The years 1917, 1918, 1921, 1923, and 1926 all show an average protein content greater than 13%. With one exception (1918), these seasons show a July temperature above 70°F. The lower protein seasons, 1922, 1924, and 1925, all show July temperatures slightly above 65°F. and relatively low June temperatures. The season of 1918 shows a protein content above 13% and a low July temperature. The rainfall for the first part of the growing season in 1918 was low, however, and of the average of 12.53 inches for the six months (March to August), 3.35 inches are recorded for August and 2.71 inches for July.

The crops of 1917 and 1926 show relatively high average protein content. The June temperature is low in both years, but these two years show the lowest rainfall for the period.

When considering the crop of the entire state, temperature is a more important factor affecting quality than rainfall. Excessive rainfall probably does not adversely affect the test weight except where temperature conditions are such that it provides more favorable conditions for development of rust. It is generally agreed, however, that excess moisture tends to lower protein content of wheat. The experiments on growing wheat under irrigation usually show a low protein content for irrigated wheat. The investigations of Widtsoe and Stewart (1920), and Stewart and Hirst (1913) of the Utah station show a relation between amount of irrigation water and protein content. Thatcher (1913), of the Washington station and Bailey (1925), of Minnesota, hase called attention to variation in protein content due to variation in rainfall in different localities.

The North Dakota station has made crop surveys for the last five years, and the data on protein content of wheat are usually averaged by counties. Using the average protein content for the county and the rainfall data from United States Weather Bureau stations, an attempt has been made to correlate average protein content and rainfall during the latter part of the growing season. The data are given in Table II.

A marked negative correlation between rainfall for May, June, and July and protein content is found for 1923 and 1925. Coefficients for 1924 and 1926 are negative and more than three times the probable error. The correlation for 1922 is negative, but is less than the probable error.

TABLE II

RELATION OF AVERAGE PROTEIN CONTENT OF WHEAT, BY COUNTIES, TO RAINFALL IN
DIFFERENT AREAS OF NORTH DAKOTA

Year	Average protein in county and rainfall for May, June, and July		Average protein in county and July rainfall	
	Coefficient of correlation	Probable error	Coefficient of correlation	Probable error
1922	−0.081	±0.113	+0.120	0.112
1923	− .585	± .088	− .296	.123
1924	− .347	± .095	− .163	.105
1925	− .608	± .068	− .009	.109
1926	−0.432	±0.098	−0.075	0.120

This indicates less relation between July rainfall and protein than exists between rainfall for three months and protein. Rainfall is evidently a factor in determining the relative protein content of wheat from different sections of the state.

General Discussion of Climatic Factors

In considering the effect of climatic factors on quality of wheat, the principal data discussed have applied to a limited area—the state of North Dakota. Can conclusions reached from a study of these data be applied to a larger area?

Sherwood (1924, 1925, 1926), of Minnesota, reports surveys on Minnesota crops for 1924, 1925, and 1926, and the average protein contents for the three years are respectively 11.50%, 11.67% and 12.74%. The average protein content reported for Minnesota wheat in 1924 was 11.50%, which was slightly higher than that reported for North Dakota—11.33%. The Weather Bureau records show slightly higher May, June, and July mean temperatures for Minnesota in 1924, which are probably counteracted by slightly higher rainfall. The average protein content of North Dakota wheat as determined through surveys was 12.30% and 14.21%, respectively, for 1925 and 1926. As compared to Minnesota, Weather Bureau records show that prevailing temperatures for May, June, and July showed no great difference, but the rainfall was significantly less in North Dakota. The higher average protein content of North Dakota wheat for these two years can therefore be attributed to less rainfall.

The Kansas crop of 1925 was very high in protein content, and hot weather in June hastened the maturity of the crop.

Table III compares the normal temperature and rainfall from several states.

TABLE III

COMPARISON OF TEMPERATURE AND RAINFALL DATA OF DIFFERENT STATES*

States	Normal temperature, degrees					Normal rainfall, inches	
						Growing season March to Aug.	Annual
	March	April	May	June	July		
North Dakota	22.6	41.7	52.6	62.8	67.5	13.15	17.94
South Dakota	30.6	45.5	55.8	66.0	71.6	14.86	20.21
Minnesota	26.3	43.2	54.9	64.9	69.5	17.78	25.97
Kansas	42.9	54.6	63.6	73.6	78.3	18.48	27.02
Missouri	43.5	55.1	64.6	73.5	77.4	23.83	39.77
Illinois	40.2	51.8	62.7	71.5	75.9	21.16	36.42
Ohio	39.8	51.1	60.8	69.3	73.6	21.49	37.97

*Data from U. S. Weather Bureau reports.

Missouri, Illinois, and Ohio are considered soft-wheat territory, and these states, as compared to the other four, show significantly higher rainfall. The mean temperatures for these states do not differ greatly from those of Kansas, but Kansas shows a consistently higher temperature than Illinois or Ohio. Winter wheat is usually harvested about the first of July, and June is therefore the critical month for the crop. Relatively low rainfall and high June temperatures are evidently responsible for the high average protein content of Kansas hard winter wheat.

Kansas has a higher rainfall than the hard spring wheat states (the Dakotas and Minnesota). The rainfall is much lower in North and South Dakota. Since hard spring wheat is harvested approximately one month later than winter wheat, the June temperature of Kansas can be compared with the July temperature of the spring wheat states. The mean normal June temperature for Kansas is 73.6°F., while July temperatures for North Dakota, South Dakota, and Minnesota are respectively 67.5, 71.6, and 69.5°F. The higher rainfall in Kansas is counteracted by the higher temperature under which the crop matures.

The Canadian Great Plains provinces are an important part of the spring wheat belt. The prevailing temperature during the summer months is somewhat lower in the Canadian provinces than in North Dakota or Minnesota, as shown by the reports of the Marine and Fisheries Department (1924), but the effect of lower temperature is counteracted by a corresponding decrease in rainfall. Owing to the lower average temperature, the Canadian provinces probably have a greater chance of producing heavy wheat, and the relatively low rainfall tends to keep the protein content high.

It is apparent that less rainfall is needed to produce a crop in the more northern latitudes, as the loss by evaporation is probably

less. Variations in temperature and rainfall profoundly affect the quality of wheat. The effect of high temperature is to increase protein and decrease test weight. Whether the detrimental effect of high temperature on test weight is direct or indirect through influencing rust development, is open to question. An increase of moisture evidently decreases the protein content. The critical period for the wheat crop is the two or three weeks immediately preceding harvest. The critical period, therefore, for the spring wheat crop is the month of July; and for winter wheat, the month of June.

Effect of Soil Fertility

The factor next in importance to climate in affecting the quality of wheat is the relative fertility of the soil on which it is produced. Seasonal variation in climatic factors cannot be controlled by the wheat grower, but soil fertility can be at least partially controlled.

Test Weight Per Bushel

Data on the effect of soil fertility and fertilizers on test weight are not extensive. Ames et al. (1912, 1917), of the Ohio station, found that applications of phosphorus increased the plumpness of the grain. Increase of nitrogen caused more shrivelled kernels.

Walster (1926), of the North Dakota station, noted an effect of the preceding crop and rotation on the test weight per bushel of wheat.

Swanson and Sewell (1926), of the Kansas station, have shown that different methods of tillage affect the test weight per bushel. Table IV gives data of the department of agronomy of the North Dakota station on the effect of the preceding crop on the test weight per bushel.

TABLE IV

EFFECT OF CROP SEQUENCE AND MANURIAL TREATMENT ON TEST WEIGHT PER BUSHEL

| | Test weight* per bushel | |
Rotation	Unmanured plots	Manured plots
	lb.	lb.
Potatoes, wheat, red clover, barley	58.2	58.2
Red clover, wheat, corn, barley	59.0	59.4
Barley, wheat, red clover, corn	59.0	60.2
Corn, wheat, red clover, oats	59.4	59.2
Rye, wheat, red clover, corn	60.3	60.2
Millet, wheat, corn, barley	61.5	61.0

*Kota wheat from rotation plots at Fargo.
Average for four years—1921 to 1924.

Wheat shows the lowest average test weight following potatoes, and the highest test weight for four years, following millet.

Fertilizers, crop rotations, crop sequence, and tillage, probably all have a definite effect on the test weight per bushel. The study of the relation of cultural methods to wheat quality has been limited and more information is needed on this important subject.

Protein Content

The protein content of wheat has been studied more extensively than the test weight per bushel. The effect of nitrate applications on wheat has been studied by a number of investigators, among whom may be mentioned Davidson and LeClerc (1917, 1918); Jones, Colver, and Fishburn (1918); Headden (1915a, 1915b); Gericke (1916a, 1916b); Ames et al. (1910, 1912, 1917); Neidig and Snyder (1922); and Sievers and Holst (1922). Results of these investigations indicate that the application of nitrates when the wheat is heading will almost invariably increase the protein in the grain.

If the supply of nitrates in the soil at heading time is plentiful the wheat will have high protein content. If nitrogenous fertilizer is applied at seeding time, the amount must be sufficient to insure a supply of nitrates to the plant until harvest time.

TABLE V

EFFECT OF CROP ROTATION SYSTEM ON PROTEIN CONTENT OF WHEAT*

| | Protein of wheat | |
Rotation System	Unmanured plots	Manured plots
	%	%
Non-legume rotations	11.29	11.22
Red clover rotations	13.20	13.08
Field pea rotation	13.62	13.33
Alfalfa rotations†	14.55	15.06
Sweet clover rotation	.....	14.02

*Data from Fargo rotation plots—three year average 1921-23.
†Three years of alfalfa.

Studies on the use of fertilizers for increasing the protein content of wheat have given valuable information, but it is improbable that the application of nitrates would pay a dividend to the grower. The nitrate content of the soil can be increased by other methods. Crop rotations and tillage have an important relation to the nitrate content of the soil and consequently to the protein content of wheat.

Swanson (1924) of the Kansas station, has shown the relation between nitrate content of the soil and protein content of wheat. Swanson and Sewell (1926) show that crop rotation and tillage influence the protein content of wheat.

Neidig and Snyder (1926), of the Idaho station, have shown that crop rotations and manure have a significant effect on the protein content of wheat.

Studies at the North Dakota station show the value of legume rotations in increasing protein content of wheat. A summary of these data is given in Figure 4, and shows that legume rotations produce wheat of higher protein content than non-legume rotations. The relative value of any rotation system in increasing protein content of wheat depends largely upon the character of the soil and the prevailing climatic condition of the regions. The data for Figure 4 were obtained with experiments on the heavy clay soils of the Red River Valley. Alfalfa and sweet clover, with their extensive root systems, have a peculiar value in improving the physical condition of heavy soil. For the lighter soils of western North Dakota, summer fallow apparently has considerable beneficial influence on protein content.
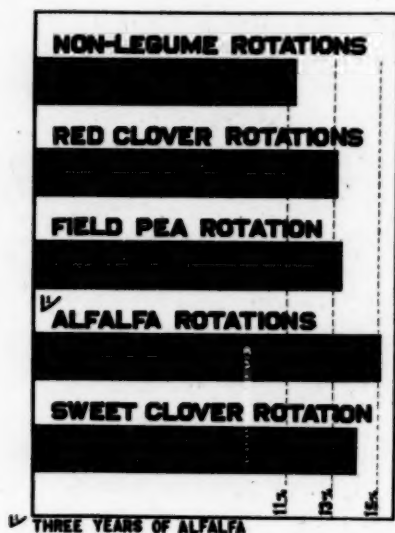
Fig. 4. Effect of Different Crop Rotation Systems on Protein Content of Hard Red Spring Wheat Grown on Fargo Rotation Plots

Summary

An attempt has been made to summarize the effect of the more important pre-harvest factors which affect the quality of wheat. These have been discussed in terms of test weight and protein content. For the sake of briefness no discussion of the effect of climatic and other factors on diastatic activity has been

included, but data collected on North Dakota wheat indicate (Mangels 1926) that the diastatic activity of spring wheat tends to vary inversely as the protein content. The variation in diastatic activity may account for the relatively low baking strength of some lots of very high protein wheat.

Preharvest factors affecting wheat quality invite further study. Certain factors are at least partially under the control of the grower, and further study of such factors should give the wheat producer a larger measure of control over the quality of the wheat produced.

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INTERPRETATION OF BAKING TESTS

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In approaching the subject of baking tests, it will be neces-
sary to confine ourselves definitely to the interpretation of a par-
ticular test. There are nearly as many baking tests as there are
operations. The tests, however, can be classified into about four
types.

In one of the common tests a so-called expansion loaf is
produced. You are probably all familiar with this type.

The second type bakes all flours under identical conditions, the
flour being the only variable. From the bread obtained in this way
an attempt is made to anticipate what the flour might do under
optimum conditions or in a commercial bakeshop.

By another type of test an attempt is made to produce the
best loaf of bread which the flour is capable of making. Condi-
tions are varied in an attempt to get optimum conditions for the
flour.

In a fourth type the previous tests are enlarged, not only to
get the best loaf of bread and to determine the conditions under
which it is produced, but also to obtain additional information as
to the ability of the flour to stand abuse and to give good results
under more or less widely varying conditions.

To this type belongs the test which we use in our laboratory,
and with which we are most familiar. We shall confine our re-
marks to the interpretation of baking tests of this type.

Before giving a brief outline of our test, it might be well to
consider what information is desired when a baking test is
made. In the case of soft wheat flours we wish to know the suita-
bility of a flour for pies and pastries, cakes, crackers, pretzels, etc.
We have not gone intensively into this work, but we are of the
opinion that information of value is obtained in baking bread from
soft wheat flours. Their suitability for the purposes mentioned
depends, partially at least, upon their relative strength and the
bread baking shows this to a fair degree.

In the case of hard wheat flours the baking test may be made
for the purpose of determining the uniformity of shipments where

the desired standard has already been tested and comparison is made with a type sample which has previously been submitted. The baking test, on the other hand, may be a general one to measure the suitability of a flour for a specific purpose. In some cases the desirability of a flour for specific purposes must be considered from the standpoint of the equipment and needs of a specific user. By this we mean that a flour may be entirely suitable for some plants and would not give satisfactory results in others. In general, flours may be classified as to their suitability for use as sponge flours, dough flours, or straight dough flours. We are considering, in this case, the use of hard wheat flour for pan and hearth breads and we shall limit our discussion to this phase of flour testing.

Hard wheat flours may be classified as weak, moderate, strong, and very strong. A weak flour will give satisfactory results under ideal conditions if the flour is carefully handled. Strong and very strong flour will give satisfactory results not only under ideal conditions but under various degrees of abuse. In a commercial bakeshop, flours may perhaps be classified under four headings.

For sponges, when the sponge and dough method is employed, a stronger flour is generally considered desirable. Such a flour usually has a protein content of 11.50% to 13.00%, depending somewhat upon the crop year and bakeshop conditions. It must be able to stand some abuse and still give good results. It need not be a short patent flour, as the long fermentation which the sponge usually undergoes will cause a certain amount of bleaching.

A dough flour which gets a rather short fermentation need not have the strength of a sponge flour. It should, preferably, be of shorter extraction and better color. Such a flour should have a protein content of 10.50% to 11.50%, depending, again, upon the crop conditions of that year and the plant which is using it.

A typical straight dough flour will be an average of a good sponge flour and a good dough flour. A protein content of 11.25% to 12.00%, a reasonably good color, and neither too long nor too short an extraction will give, as a rule, the best results.

Occasionally, flours nearly unsuited by themselves, will produce good bread commercially when used in a blend. An example of this is the flour made from Bluestem wheat which is blended with Montana or other strong flour with excellent results. Such flour, if used alone, will usually be unsatisfactory as a pan bread flour. A flour may be too strong for use in straight doughs alone but may give quite satisfactory results when blended with a weaker

flour. In general, however, for use in straight doughs, a blend of
a very strong and a very weak flour is to be avoided. Better results
will be obtained if a blend of two different types of flour, e.g.,
spring wheat and southwestern wheat is desired, by using flours of
somewhat similar characteristics. In this regard it might be men-
tioned that suitability of flours for specific purposes depends not
only upon the equipment of the user but also upon the type of
bread to be produced. In markets requiring a spongy, voluminous
loaf, a very different flour is needed from that which is entirely
satisfactory in parts of the country where a compact, close grained
loaf is in favor.

In making our baking tests we have adopted a method which
approaches actual baking practice as nearly as possible and the
loaves produced are commercial loaves in size, shape, and other
characteristics. We use a plain straight dough formula, calling
only for flour, water, yeast (2.30%), salt (1.75%), sugar (3.00%),
lard (2.00%), and a very small amount of a simple yeast food,
used to correct the deficiencies of our local water and to level the
differences in the mineral content of waters in different lo-
calities. The sugar, salt, and yeast food are added in the form of
a solution, a definite quantity of solution being used for each
bake. The dough is brought to the proper absorption by adding
the required amount of water.

The preliminary absorption of a flour is determined by as-
certaining the moisture on the flour, if the type of flour is known,
and calculating the correct absorption from our experience with
that type of flour. We also make a small dough ball, using 50
grams of flour. The final adjustment is made in the mixer.

Seven hundred grams of flour and the ingredients mentioned
above are mixed into a dough, in a high-speed Bachman mixer,
the mixing being interrupted before the full mixing time in order
that the absorption of the dough may be corrected, by adding either
flour or water as the appearance of the dough indicates. Two
550-gram doughs are scaled from this large dough and fermented
at 81° F., the time of fermentation depending upon the type of
flour, if known, and upon the appearance of the dough as fermen-
tation progresses. One of these doughs is given what we consider
a normal fermentation, the other is fermented for half an hour,
more or less, depending upon the characteristics of the flour.

Molding is done in a commercial machine. It is our ex-
perience that uniform molding is the most difficult and one of

the most important items in a baking test. We are thoroly convinced that hand molding will not give the same uniform loaves that machine molding produces.

The dough is placed in a commercial one-pound pan and proofed at 95° F. until the correct proof, determined by the appearance and feel of the dough, has been obtained. It is then baked, cooled for an hour in the laboratory, and stored over night in a closed cabinet.

Each day a series of loaves is baked, using our standard flour, and all loaves are compared with these. Our standard flour is a short patent moderately bleached flour of good strength and quality. It is usually a blend of spring wheat and Kansas flour. The standard bake gives a check on the condition of the yeast used and on the correctness of our baking solution.

The first step in interpreting a baking test is to determine whether or not the flour has had a fair chance to show optimum results. A careful record has been kept of the behavior of the dough during fermentation. If the dough has tightened up or slackened, it is usually necessary to repeat the test, making the required adjustments in absorption. A careful inspection of the loaves resulting from a long and a short fermentation shows whether or not the flour has received the proper fermentation treatment. If neither of the two loaves is satisfactory, it is necessary to repeat the test, making the proper adjustments in fermentation.

The important points to consider in judging a test loaf are: measured loaf volume, oven spring, shape, bloom, grain, texture, color of crumb, flavor, and odor.

Loaf volume gives a good indication of the strength of the flour. A voluminous test loaf indicates a strong flour, providing that the oven spring, grain, and texture are good. If the long-fermentation loaf is the larger of the two, a stronger flour is indicated than when the short-fermentation loaf shows up best.

The oven spring, or break, also is a valuable indication of the strength of a flour. The break should be bold and shreddy and show no signs of shortness, tearing, or splitting. Lack of oven spring or a ragged break indicates a weak or possibly a green or freshly ground flour.

A comparison of the long- and short-fermentation loaves·is of great value. If the short-fermentation loaf shows good volume and a bold, shreddy break, and the long-fermentation loaf shows less volume and a ragged or torn break, it indicates that the

flour is sound and of good quality but of moderate strength, and that care must be taken not to give it too long or too vigorous a fermentation. Such flour is best used as a dough flour, or blended with stronger flour for use in straight doughs.

A flour which produces bold, voluminous test loaves on both the long and the short fermentation, indicates strength and good stability. A flour of this type will stand considerable abuse and is well suited for use as a sponge flour or in straight doughs where a large, spongy, soft-feeling loaf is desired.

When the short-fermentation loaf appears to be gluten bound and a very-long-fermentation loaf shows good quality, unusual strength is indicated. Some high-protein Montana and Canadian flours show these characteristics. Flours of this type are best used as sponge flours or in hearth bread or in a blend with flours of lower strength.

There is also a type of flour which is softer than the usual run of hard wheat flour, which will give very similar test loaves on both the long and short fermentation. These loaves are of moderate volume and the break is not exceptionally bold, but the grain is unusually close. Such flours are best used to produce the close-grained compact loaves which are in favor in certain markets.

The bloom of the test loaves should be noted if it varies markedly from the normal. It is impossible under laboratory conditions to show slight variations in bloom-producing qualities, but any large deviation should be noted. A pale, sickly bloom indicates an over-bleached or otherwise damaged or defective flour. Clears and the longer extraction flours usually show a deeper bloom than the shorter extraction flours. The bloom of the test loaves is to a certain extent a check upon other characteristics.

The grain of the test loaves should receive careful consideration. It should be close and uniform with thin-walled, slightly elongated cells. An open grain may indicate a damaged flour or it may show improper fermentation. The grain is a valuable means of determining whether or not the test loaves have been properly fermented. Certain flours, even under optimum conditions, will show a tendency toward holes. Such flours invariably cause trouble in the commercial bakery. This condition has been especially prevalent with flours from this year's crop.

The texture of the test loaves should be smooth and silky. A harsh and lumpy texture, provided the fermentation treatment has

been correct, indicates a damaged or unsound flour. A comparison of the texture and grain on the long and short fermentation test loaves gives a valuable indication as to the stability or fermentation tolerance of flour, or, in other words, its ability to withstand variations in fermentation.

The color of crumb, taking into consideration the grade or extraction of the flour, is also of considerable importance. A clear, bright, creamy white color is by far the most desirable; dull gray is decidedly objectionable. A dead white may be satisfactory but there is always the possibility that upon prolonged storage the color may become gray. A bright, very creamy tinge is not undesirable on a freshly milled flour, as such a flour will bleach out considerably upon aging. A yellow color is, of course, not desired except in localities where the sale and use of bleached flour is not permitted.

The test loaves should also be examined for flavor and odor, noting any indications of mustiness or other foreign odors. A flour which contains sufficient mold to be noticeable in the baked loaf is, of course, unfit for use. Unsound, damaged or over-bleached flours usually have a characteristic "off" flavor and odor.

Certain chemical data are of value in properly interpreting or checking the baking test. Determinations of ash and acidity give an indication of extraction. Protein gives an indication of the strength of the flour. A moisture determination is of value, so that all data may be calculated to, and reported on, a uniform moisture basis. Chemical data alone have little value in judging the quality of a flour. The most important test is the baking test.

A careful inspection of the test loaves in the manner which we have just described will determine not only the character of the flour under optimum baking conditions, but will also give an excellent idea as to the performance of the flour in the shop. Information on this point is, in our estimation, the prime objective of the baking test. If it can be obtained by a simpler method than ours and under easily controllable conditions, we should welcome such simplified procedure without hesitation.

SURVEYING THE NEW WHEAT CROP

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(Read at the convention June 3, 1927)

Wheat is a cereal of such great importance that both the total quantity produced and the character of the grain are prime factors in determining the prosperity of the wheat-growing areas and contiguous territory, and have a marked influence upon the business conditions of the country at large. Large variations in the character of wheat occur from year to year, owing principally to changes in environmental influences. Because of these facts, attempts have been made for many years to estimate the total yield of wheat of any given crop before that crop has been harvested and marketed. Much valuable and useful information has been collected and disseminated by various governmental and commercial organizations for the benefit of all industries which are directly or indirectly concerned with the production, shipping, marketing, storage, and utilization of wheat.

The information collected is related largely to yields of wheat, with little attention paid to quality except that which may be indicated by reference to damage by rust, by insect infestations, by drouth, or by flood. References to the quality of the wheat are usually very general in the majority of reports on the condition of a crop, and rarely, in most sections of the wheat-growing areas, is information available concerning the specific factors which the cereal chemist knows are most important in determining the milling and baking value of the wheat.

Coincident with the progress along scientific lines in milling and baking, has come a demand for more exact knowledge of the milling and baking characteristics of the wheat of a new crop, and it is almost imperative that this information be ascertained very soon after harvest. Promptness in completing a wheat survey measures to some extent its value.

These remarks will indicate the opportunity, or may I say the necessity of making a survey of the wheat crop before the wheat actually begins to flow through marketing channels.

Of the factors or characteristics of the wheat kernel which are indicative of its usefulness or desirability for milling and baking

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purposes, the following deserve consideration: weight per meas-
ured bushel, protein or gluten content, moisture content, ash con-
tent, enzymic activity (diastatic and proteoclastic), soundness, dock-
age, foreign matter (including other cereals and inseparable weed
seeds), smut, garlic, heat damage, mustiness, presence of weevils
or other insects, and, finally, laboratory milling and baking tests.

All the factors mentioned have an influence upon the market
value and milling value of wheat. Certain of them cannot be meas-
ured in any exact way in a survey at the time of harvest. These
will be eliminated from the discussion first. Obviously, we cannot
consider most forms of damage—heat, mustiness, infestation with
weevils or other insects. Dockage and foreign matter may or may
not be estimated, depending upon the conditions under which the
samples of wheat are taken. These are of comparatively little
importance, anyway, as an indication of wheat quality. Smut and
garlic can be estimated to some extent if the examination is re-
stricted to samples which have been harvested, threshed, and de-
livered or are ready for delivery to the elevator. The determina-
tion of the extent of damage due to sprouting also depends largely
upon the conditions under which the samples are collected, and
the results would be reliable only when the examination was made
upon samples delivered to the country or terminal elevators. Dam-
age due to sprouting usually results from post-harvest and pre-
threshing rainfall, and when a survey is made at harvest time the
sound condition of wheat may not be an index of its condition after
exposure to weathering for several weeks. For example, the wheat
produced in certain sections of Minnesota in 1926 gave promise of
grading No. 1 hard spring, but adverse weather conditions prevailed
at harvest time, and the excessive rainfall which followed the
ripening period, in some cases before the grain could be harvested,
caused severe damage. As a result, much wheat which was other-
wise No. 1 grade was degraded on account of high moisture con-
tent and damaged kernels. This fact is proof that too definite
conclusions regarding soundness should not be drawn from the
results of a survey. These remarks apply also to heat damage
and mustiness.

Moisture content of wheat is an extremely important factor.
Because wheat normally dries out to some extent between har-
vesting and shipping to market, and because abnormal conditions
may cause an increase in moisture content after harvest, moisture
determinations made upon wheat samples collected at harvest time

may bear no relation to the moisture content of wheat received in the milling centers. Therefore it appears of little value to include this determination in a survey.

Diastatic activity, while serviceable in showing the enzymic deficiencies of certain wheats, is not a determination which with our present time-consuming methods is well suited to such a survey as is considered here.

If you still have in mind the dozen or so items which I indicated a few moments ago as of importance in estimating the value of a wheat crop, you will note that we have eliminated all but four—protein content, weight per bushel, ash content, and actual laboratory milling and baking tests.

Protein content has been chosen as one of the tests in a wheat survey for several reasons. No other single determination yields as much information concerning the quality of wheat, especially of the baking properties. The importance of a knowledge of the protein content of wheat from the marketing viewpoint has been rehearsed too many times to require reiteration here. With modern laboratory facilities, protein content can be determined accurately and rapidly in large numbers of samples. The physiological development of the wheat kernel, as far as nitrogen complexes are concerned, is practically complete at the time of harvest. No marked change in the quantity of nitrogen after harvest can be anticipated. With proper allowance for the moisture content of the kernel, the protein content can be determined at harvest with sufficient accuracy to serve as an index of the percentage of protein in the same wheat as shipped to market several weeks or months later. The great variability in protein content of different lots of wheat grown under different conditions justifies the significance we attach to this determination for survey purposes. In the surveys made in Minnesota, protein content of individual samples has ranged from 8% to 18%, while averages of samples by counties showed variations from 10% to 15%.

Weight per bushel probably ranks first in importance as an index to the milling value of wheat, owing to its influence on the yield of flour. Consequently this determination provides useful information for the grain trade and forms an important part of a survey of the wheat crop. As with protein determinations, we must know whether the results obtained with freshly harvested wheat are reliable or misleading, for these results are accepted as an index of the weight per bushel of wheat shipped from any given

point later in the season. The influence of the moisture content upon test weight must be recognized in a study of weight per bushel.

Wheat crops vary in ash content. This variation from year to year is sufficient to affect the ash content of any particular grade of flour. For this reason the ash content of wheat should receive consideration in setting standards for the grades of flour to be manufactured from each season's crop. Ash determinations in wheat can be readily made in a survey.

Even after numerous chemical and physical tests of wheat have been made, we must concede that milling and baking tests are necessary to determine certain characteristics of wheat flour which we have as yet been unable to measure in other ways. Among tests which are suitable for a survey, milling and baking tests cannot figure so prominently if the survey is extensive, because of the large expenditure of time required. They can be used to best advantage by testing composite samples of wheat prepared by mixing small samples gathered in definite localities of the wheat-producing areas. Such tests will serve to indicate the average baking characteristics of the localities represented, and with proper allowance for the variations between laboratory-milled and commercially-milled flours, as well as allowance for the changes in baking properties which are known to take place during storage of wheat, considerable valuable information can be obtained.

I have cited the determinations which appear to be most valuable in indicating the characteristics of a new wheat crop, as viewed from the standpoint of a survey designed to provide information just as soon as possible after the wheat is ripe.

If milling and baking value, economic or merchandising value, and feasibility of testing are all considered, these determinations will rank in importance as follows; protein content, weight per bushel, laboratory milling and baking tests, ash content. In outlining a program for a survey, the limitations imposed by available time and funds will control the extent to which these determinations can be employed.

No test of a material is reliable unless the sample tested is truly representative of the whole from which it was taken. The importance of obtaining representative samples in a wheat survey cannot be overemphasized. A carefully drawn plan for sampling must be employed. Samples gathered here and there in haphazard fashion are unsuitable. Samples mailed by interested individuals

are frequently of doubtful value largely because it is a natural human tendency to select the best and not the poorest wheats.

In the recent surveys of Minnesota wheat crops, selections of the number of samples and of the localities to be sampled have been based largely upon the estimated wheat acreage for the state. Samples have been collected from shocked grain and at threshing machines. Upon shipment to the laboratory the wheat heads were dried, threshed, cleaned, and ground. Protein determinations were made on the dry basis, after which calculations were made to the basis of 13.5% moisture. The individual results were grouped in order that the mean protein content of wheat produced at different points could be estimated. Plotting of the results upon the map of the state served to present the data in graphic manner.

A few comparisons drawn from records of the Minnesota Experimental Flour Mill will show the relation between the protein content of Minnesota wheat as indicated by the surveys and as found by the testing of carlot samples of wheat.

Survey of the 1924 crop showed an average protein content of 11.50%, while carlots of the same crop received at the Testing Mill averaged 11.69%. The 1925 crop survey showed an average of 11.67%, in comparison with 11.79%, the average of carlots received at the Testing Mill. These results show close agreement each year between the survey average and the carlot average.

When the 1926 crop as surveyed and as shipped to market is considered, the agreement is good, but not so close. The average protein content shown by the survey was 12.74% (corrected to 13.5% moisture). The average protein content of 3900 cars received in the Minneapolis market, as tested by the Minnesota Grain Inspection Department, was 12.40% (uncorrected). Moisture records are not available for all these cars, but judging from the records of the State Testing Mill the average moisture content of Minnesota wheat of the 1926 crop exceeded 13.5%, possibly approximating 14.5%. Correction to the same basis as the survey' average would show that the carlot average differed only about 0.25%. In the absence of a more detailed study of protein records, the figures reported here may be taken as evidence of the reliability of results obtained in a wheat survey.

Summary

Survey of the wheat crop immediately following harvest will provide valuable information concerning the character of the wheat prior to the movement to market of large quantities.

Protein content, weight per measured bushel, and ash content are determinations which can be most readily utilized in a survey organized to obtain data concerning wheat quality. Laboratory milling and baking tests of composite wheat samples are very useful when it is feasible to include them.

Comparisons of protein content of Minnesota wheat as surveyed at harvest time and as marketed during the months following have shown close agreement for the crop years 1924, 1925, and 1926.

THE ROLE OF PHOSPHATES IN BREAD MAKING[1]

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(Read at the Convention June 2, 1927)

In a discussion of the use of phosphates in the baking industry, two major considerations are involved, namely, the extensive use of acid phosphates as the acid ingredient of chemical leavening agents, and the use of various phosphates in the production of yeast leavened bread. A study of the first application must of necessity include a consideration of the rate of reaction of acid phosphate with sodium bicarbonate and the influence of the resulting compounds upon the constituents of the dough. Such applications of phosphates to baking will not be discussed in this paper. It will be confined to the discussion of the various hypotheses and the observed facts relative to the use of phosphates in the production of yeast leavened bread.

In this latter connection it appears that ordinary dosages of phosphates may exert two types of effects (a) upon the colloidal

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properties of the dough, and (b) upon the yeast activity and reproduction as reflected in the rate of alcoholic fermentation. A further limitation will be made to the part played by mono calcium phosphate in so far as this discussion of the subject is concerned.

Wood (1907) was the first to attempt to account for the properties of wheat gluten on the basis of the effect of acids, bases, and salts. Crude gluten obtained by washing was immersed in various acid solutions and in similar solutions to which varying quantities of salts had been added. He recorded in graphic form the concentration of several acids which dispersed the crude gluten, and in the same connection indicated the concentration of a particular salt which prevented dispersion. Wood's researches gave tremendous impetus to the study of gluten properties as related to environment and other conditions. His work advanced far enough to result in evolving a chemical hypothesis for the loss of coherence in gluten when treated with dilute acids. He postulated that the dispersion of the gluten was in consequence of the formation of protein salts which are ionized in aqueous solution. These ions, or aggregates, acquire electric charges which result in their dispersion in water. Coagulation of the dispersed protein can be accompanied by a reduction of the magnitude of this charge. The salts with which he worked would effect such a reduction of charge and hence cause coagulation to an extent which is conditioned by the concentration of the acid and also by the ions contributed by the salt.

Among other salts, Wood used sodium phosphate, and Na_2HPO_4, and found that relatively small concentrations would inhibit or prevent the dispersion of the gluten with hydrochloric acid. In this respect the phosphate was less effective than the sulphate of the same alkali metal and was about equally as effective as the chloride. Magnesium sulphate was more effective than sodium sulphate and aluminum sulphate was still more effective.

The attention of Wood was particularly attracted to the effect of phosphates because of the presence of compounds of phosphoric acid in ordinary wheat flour. In a later contribution, Wood (1913, p.72) states, "After making a great many analyses it was found that the amount of soluble phosphate in a wheat was a very good index of the shape and texture of the loaf which it would make. The toughness and elasticity of the gluten no doubt depend on the concentration of the soluble phosphate in the wheat grain, the more the soluble phosphate the tougher and more elastic the gluten, and a tough and elastic gluten holds the loaf in shape as it expands in

the oven, and prevents the small bubbles of gas running together into large holes and spoiling the texture."

Upson and Calvin (1916) and Gortner and Doherty (1918) likewise observed that potassium phosphate would depress the water-imbibing capacity of gluten. Upson and Calvin found K_2HPO_4 somewhat more effective than the KCl in reducing the swelling of gluten in lactic acid, while Gortner and Doherty did not observe any great difference between the effects of the two salts. Magnesium sulphate was more effective than either of the two salts before mentioned.

Wood also observed that the degree of turbidity of aqueous extract of flour was correlated with the concentration of soluble compounds of phosphoric acid and suggested a measure of turbidity as an index of gluten properties and baking strength.

While the contentions of Wood have not been wholly accepted or supported by subsequent work, the fact remains that his observations suggested an entirely new line of attack on the vexing problem of flour strength. His work may accordingly be regarded as the classic study in this field of wheat research.

That much the same view of the significance of phosphates was entertained by other workers in this field was evidenced by the fact that Humphries (1907) in British Patent No. 13,135 specified: "Affecting the physical properties of the flour so that the dough may be improved. For this purpose in some cases, and when the stock is under treatment, water may be used, while in other cases the stock or flour may be sprayed with a solution of appropriate mineral salts such as salts of potassium, calcium or magnesium, or an acid such as phosphoric acid may be used." (page 5, lines 19-24). In another portion of the same specification he details one of the purposes of his process, "To improve the dough, the stock or flour may be sprayed with a solution of phosphate of magnesia made soluble by addition of phosphoric acid, of soluble phosphate of lime. or potassium phosphate, or of a mixture of any of these, until the stock or flour has received about 0.2% of its weight of the salt or salts."

Chitty and Jago (1909), in British Patent No. 22,434, likewise refer to the effect of substances of this type upon the properties of dough when they state (page 3, lines 16-18) "The flour from wheat which has been treated with phosphoric acid or the before-named salts is characterized by improvement in the toughness and working qualities of the dough made therefrom." The salts to which

reference is made in this quotation are the phosphates of calcium,
magnesium, and potassium, as well as magnesium sulphate.

In many instances the statements respecting the effects of
phosphates upon the physical properties and colloidal behavior of
dough are not accompanied by data to establish the contentions.
This is not surprising in view of the difficulties involved in quanti-
tatively measuring the properties in question. Bailey and LeVes-
conte (1924) made use of the Chopin extensimeter in an effort to
measure the effect of adding the equivalent of 0.125% of calcium
acid phosphate to a plain flour-water dough. The extensibility of
the phosphated dough was 5.6% greater than that of the control
dough with which it was compared. This is not a very large in-
crease in extensibility, especially as the probable error may amount
to from one-fourth to one-fifth of this difference.

Earlenbaugh (1926) added dry calcium acid phosphate in
varying proportions to flour and then leached this flour with two
portions of distilled water, acidulated the leached residue, and
determined its viscosity. Two concentrations of flour were used,
which made it possible to determine the tangent of the angle
formed by plotting the logarithm of viscosity against the logarithm
of flour concentration. In this manner the quality constant b of
Sharp and Gortner (1923) could be computed. No effect upon this
quality constant b could be detected in consequence of the previous
treatment of the flour with acid calcium phosphate.

A procedure was developed by Bailey and Johnson (1924) for
determining the gas-retaining capacity of yeast leavened doughs.
It was believed that in this manner differences in the colloidal be-
havior of doughs could be detected in so far as these are reflected in
the capacity of the dough to retain the carbon dioxide of fermenta-
tion. In general, doughs which are characterized as "strong" retain
a larger proportion of the gaseous carbon dioxide than the weak
doughs.

This apparatus and method were used in an effort to determine
the effect of added acid calcium phosphate upon gas retention. No
substantial effect upon this property of dough could be detected
when dosages of phosphate equivalent to 0.4% of the flour were
added to a simple yeast dough. This is evident from the data
recorded graphically in the figure. The rate of gas production in
the phosphated doughs was accelerated somewhat and reference
will be made to the magnitude of this effect in another section of
this paper.
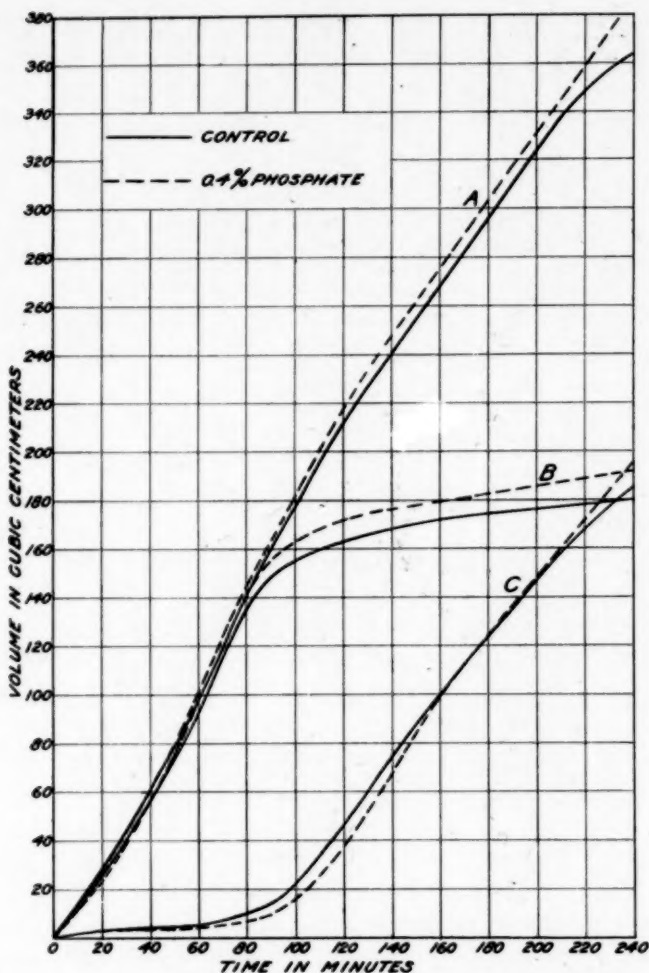
Changes in Volume which Occur in the Fermentation of a Phosphated and a
Non-phosphated Dough

Curves A represent the sum of the increase in volume of the dough and the volume of
carbon dioxide lost from the dough; Curves B, the increases in volume of the dough; and
Curves C, the volume of carbon dioxide lost from the dough.

Bearing upon this same general type of experimentation are
the results obtained by the use of another type of instrument. A
recording watt-meter was employed in the effort to determine
whether or not the superimposing of phosphate upon a dough
would be accompanied by any substantial modification of the de-
gree of plasticity. The plasticity of the dough was measured by

the consumption of power in a small dough-mixing unit as indicated by a recording watt-meter. While the results of individual observations were somewhat variable, sufficient data were secured to indicate that there was no appreciable difference in the "tightness" of doughs containing varying quantities of phosphate (up to 1%) in comparison with a control, or non-phosphated, dough. The equipment available at the time these observations were made was not ideal for this purpose and further experimentation along this line is contemplated.
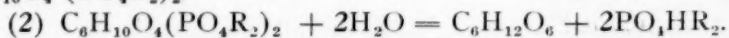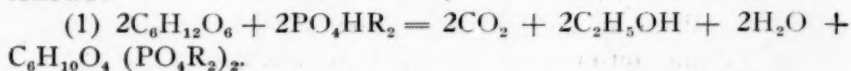
Still another attack was made upon this problem through the use of the plastometer. The instrument used was essentially of the type developed by Kelly (1925). Without entering into a detailed description of the procedure or the results obtained, suffice it to say that there was no evidence from these studies that quantities of phosphates equivalent to 0.6% of the weight of the flour resulted in any appreciable modification of the plasticity of the suspension of such flour in water.

These observations, together with a survey of the data recorded in the literature, lead to the conclusion that the effect of acid calcium phosphate (within the range of concentration of 0.2% to 0.5%) upon the properties of dough is not of large magnitude. Attention is called to the fact that the measurement of the effect of phosphates must finally be determined upon the dough itself rather than upon a crude gluten preparation that has been washed out with distilled water and hence is nearly devoid of other electrolytes. The salts originally present in the flour, in tap water, and deliberately added as a portion of the dough formula, function in the same general direction as do phosphates in establishing a coherent condition of flour gluten and hence of dough. Our observations indicate, however, that such effects upon the dough as can be detected and measured are all in the direction of improving the qualities.

Phosphates and Alcoholic Fermentation

As the earlier analyses of yeast cells revealed the presence of compounds of phosphorus, it followed that phosphates were included in the nutrient media employed in the propagation of this organism. The rôle of phosphorus in fermentation and particularly in the functioning of zymase was detailed by Harden and Young (1906). They proposed an equation representing the progress of alcoholic fermentation which involved the formation of a hexosephosphate coincidentally with the production of carbon dioxide

and alcohol. This hexosephosphate then undergoes a hydrolytic cleavage, yielding the hexose and the original phosphate. These substances are then free to enter into another series of reactions and thus the phosphate present may function in a succession of reactions. The two reactions thus involved are represented as follows:

(1) $2C_6H_{12}O_6 + 2PO_4HR_2 = 2CO_2 + 2C_2H_5OH + 2H_2O + C_6H_{10}O_4 (PO_4R_2)_2$.

(2) $C_6H_{10}O_4(PO_4R_2)_2 + 2H_2O = C_6H_{12}O_6 + 2PO_4HR_2$.

The seeming difficulty in explaining why it is that one of the two molecules of glucose appearing in the left-hand member of the first equation should undergo decomposition into carbon dioxide and alcohol while the other becomes associated with the phosphate in the form of a hexosephosphate, may possibly be found in the assumption that sugar in the solution exists in two or more forms. One form may go in one direction, a second form in another direction, but both of the forms reappear when the hexosephosphate is hydrolyzed again to hexose. Ivanoff (1907, 1909) and Lebedeff (1911, 1912) contributed to this hypothesis of the appearance of phosphoric acid compounds in the fermentation reactions and the last-named investigator suggested another and somewhat more involved series of reactions in which this substance appeared. He apparently succeeded in isolating and identifying a number of derivatives of the hexosephosphate, thus establishing its presence in the reaction mixture.

Whether or not the hypothesis of Harden and Young explains the rôle of phosphates in an exact manner, the fact remains that the addition of phosphates to a nutrient solution in which such substances were not originally present will accelerate fermentation in the presence of normal living yeast cells or in contact with a zymase preparation. The presence of phosphates in the nutrient media suggested by Hansen, Mayer, Laurent, Hayduck, Cohn, Guillermond (1920) and Willstätter and Steibelt (1921), lends emphasis to the current opinion that the propagation of yeast is at least facilitated by the presence of the phosphate ion. It is also of interest to note that the Hayduck patent (1923), under which one of the large producers of yeast is reported to be operating at the present time, includes phosphate as one of the constituents of a suitable yeast nutrient solution for the propagation of yeast. Intact yeast cells evidently respond less to small additions of phosphates, when their response is measured in terms of the rate of production of carbon dioxide and alcohol, than is the case when a phosphate-

free preparation of zymase is brought in contact with phosphates. This has been explained in a variety of ways, but chiefly upon the assumption that the intact yeast cell already contains an appreciable quantity of phosphoric acid derivatives which may function in the reactions involved in alcoholic fermentation within the cell.

In the first part of this paper reference was made to the use of the method devised by Bailey and Johnson for measuring the production in and loss of carbon dioxide from a fermenting bread dough. In applying this method to a study of the effect of added phosphates upon fermentation, it became possible to measure the relative rate of fermentation in the dough as evidenced from the increase in the volume of the dough. Studies thus conducted indicated that 0.2% and 0.4% of calcium acid phosphate increased this rate of carbon dioxide production. It has previously been indicated that such dosages of acid phosphate did not appreciably affect the rate of loss of gas from the dough. It accordingly followed that toward the close of the fermentation period the doughs containing phosphate were larger in volume than the control or non-phosphated doughs. Larger dosages of acid phosphate apparently tended to impair the gas-retaining capacity of the dough and thus to counteract the tendency toward a greater increase in expansion or volume of the dough. Typical data are recorded in the figure, which indicate the direction and magnitude of the effect of the added phosphate. Johnson (1923) likewise observed that the rate of gas production was increased in doughs to which mono calcium phosphate had been added, in contrast with the control, or non-phosphated, doughs.

These investigations did not serve to indicate whether the effect of phosphates in increasing gas production in the dough was a consequence of an increased activity on the part of the yeast cells added in the original dough formula, or to increased rate of reproduction of yeast cells in the dough, which would thus result in a larger number of active cells toward the close of the fermentation period. To throw further light upon this problem, a series of experiments was undertaken to determine whether or not there was an increase in the number of yeast cells in phosphated and non-phosphated doughs. A modification of the method suggested by Turley (1924) was employed in counting the yeast cells in the freshly mixed doughs and in doughs which had been fermented for 160 minutes. As will be observed from the data recorded in Table I, there was apparently no change in the number of cells in the control, or non-phosphated, dough, whereas it so chanced

that there was a small decrease in the number of cells in the dough to which 0.4% of phosphate had been added. Whether or not the number of cells regularly decreases in phosphated doughs is doubtful, but in any event these data give evidence of no increase during the 160-minute fermentation period, at least. From this it may be concluded that phosphate in dough results in an increased rate of gas production, not because of an increase in the number of functioning cells but rather because of the greater activity of each cell in fermentation.

TABLE I .

MEAN OF NUMBER OF YEAST CELLS PER 5 x 10⁻⁹ GRAMS OF DOUGH

	First trial	Second trial
Control		
When mixed	13.81 ± 0.26	12.55 ± 0.28
After 160 min. fermentation	13.62 ± 0.40	12.65 ± 0.37
Control plus 0.4% phosphate		
When mixed	14.78 ± 0.86	12.77 ± 0.26
After 160 min. fermentation	13.17 ± 0.16	11.80 ± 0.36

Calcium Acid Phosphate and Baking Quality

Earlier in this paper an effort was made to trace the direction and magnitude of the effect of calcium acid phosphate upon the properties of bread doughs. These effects ultimately register their useful characteristics in terms of the quality of the finished loaf. It is evident from the literature that other investigators have detected the useful function of various compounds of phosphoric acid in bread production. The references to the inclusion of phosphates in various flour and bread improver combinations appear in the patents and publications of Humphries (1908), Remington (1914), Levin (1913), and others.

While Masters and Maughan (1920) observed a small decrease in the volume of loaves when 1% of acid calcium phosphate was included in the formula, they detected a whiter color in the bread made from the phosphated dough. It should be noted that the dosage of phosphate used by them is at least double that which is ordinarily recommended when acid calcium phosphate is used as a flour improver.

In our experiments dealing with the effect of acid calcium phosphate upon the general baking properties of dough, the phosphate was added in varying proportions to a series of doughs in increments of 0.2% to 1.0%. The flours used were straight grade flours milled in the Minnesota State Experimental Flour Mill from Northwestern hard spring wheat. The previous survey of the literature

indicated that in commercial practice, dosages of acid calcium phosphate of 0.2% to 0.5% had been suggested. When we used quantities in excess of 0.5%, no improvement in baking qualities of the loaf was noted except in one particular—that of the color of crumb. Thus, with 0.6% the bread properties were similar to those of bread produced from control, or unphosphated, dough except that the crumb of the loaf was distinctly whiter. Increases in the dosage of phosphate in the dough above 0.6% tended to impair baking qualities; with 0.2% and 0.4% of acid calcium phosphate in the ordinary straight dough formula, a general improvement was evident. This registered in terms of the rate of fermentation the "liveliness" of the dough as appeared on handling it, and also in terms of the grain, texture, volume, and color of the finished loaf. No exceptions to this general statement have been noted in instances of the flours included thus far in these comparative baking trials.

In the foregoing paragraph it is noted that the rate of fermentation is accelerated when phosphates are included in the dough formula. Previous observations have led us to the conclusion that the adjustment of fermentation period must be made more carefully with weak flours. Unsatisfactory results from the inclusion of phosphate in a weak flour dough may accordingly result if a proper adjustment of the fermentation period is not effected.

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